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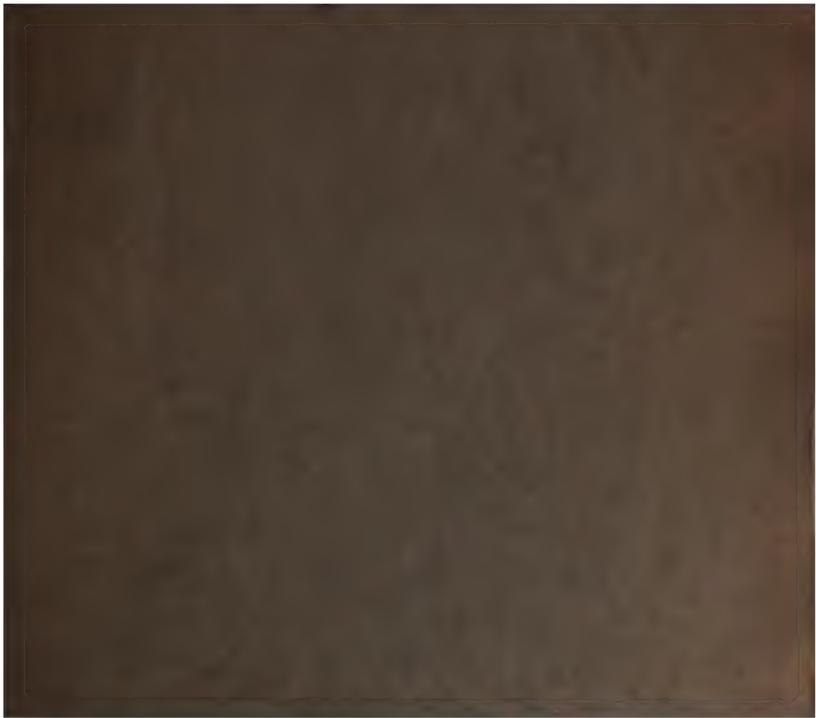
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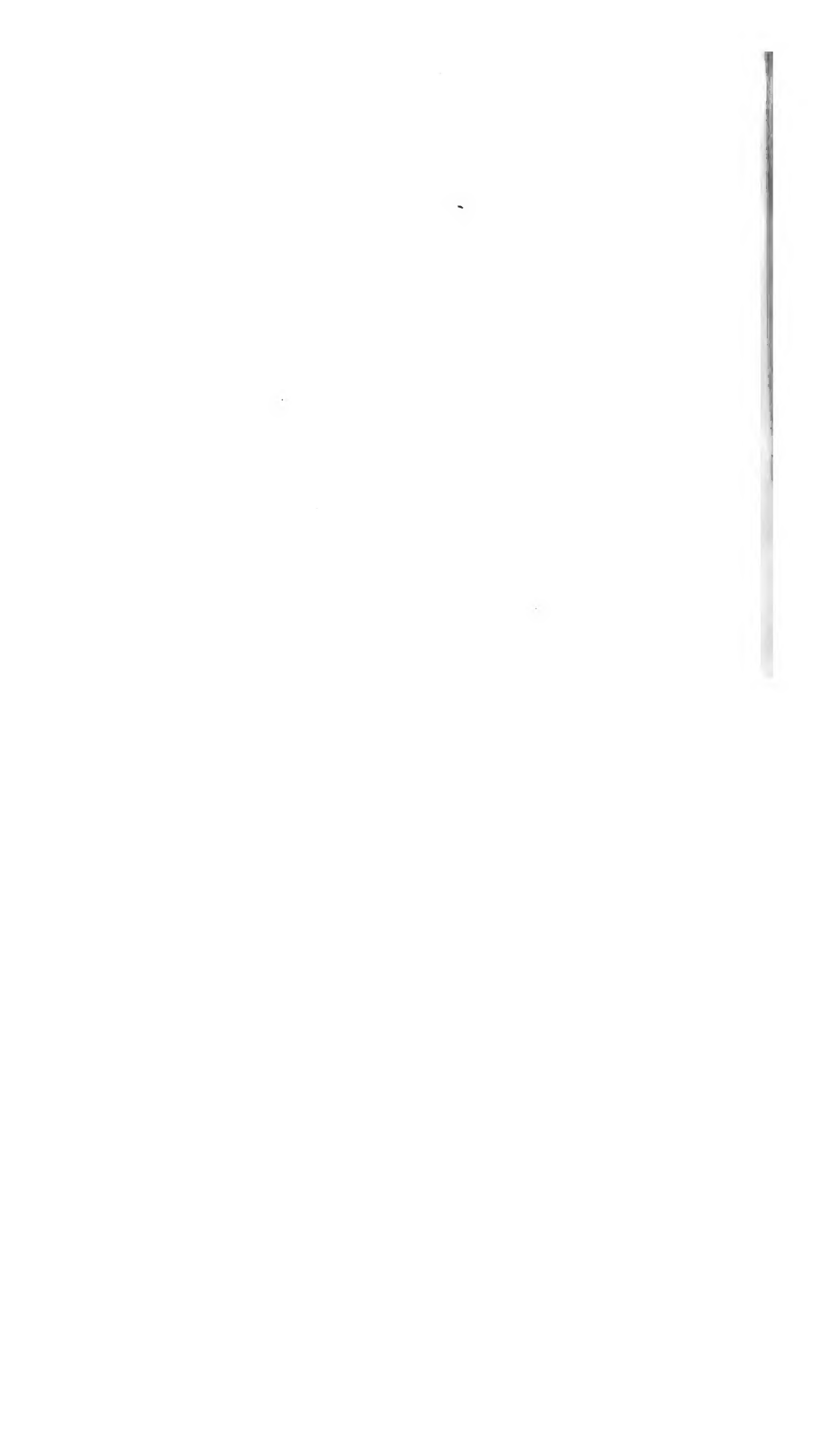
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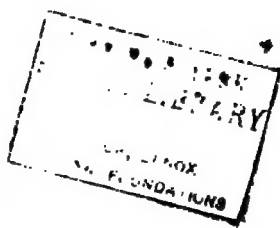
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MANUAL OF CHEMISTRY, THEORETICAL AND PRACTICAL.

REVISED AND CORRECTED

BY

HENRY WATTS, B.A., F.R.S.,

EDITOR OF THE JOURNAL OF THE CHEMICAL SOCIETY; AUTHOR OF
"A DICTIONARY OF CHEMISTRY," ETC.

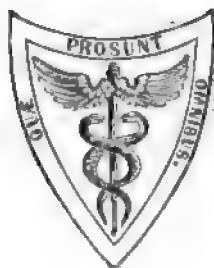
A NEW AMERICAN FROM THE TWELFTH ENGLISH EDITION.

EDITED BY

ROBERT BRIDGES, M.D.,

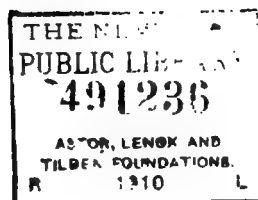
PROFESSOR OF CHEMISTRY IN THE PHILADELPHIA COLLEGE OF PHARMACY.

WITH ONE HUNDRED AND SEVENTY-SEVEN ILLUSTRATIONS.



PHILADELPHIA:
HENRY C. LEA.

1878.



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AMERICAN PUBLISHER'S ADVERTISEMENT.

THE very considerable increase in the size of this work, caused by the elaborate revision of Mr. Watts, has led to its division in England into two volumes, which appeared at an interval of several months. In reprinting it, by the use of a small but exceedingly clear type it has been compressed into one volume, which, it is hoped, will be found not unhandy for study and reference. While no omissions have been made, the American editor has felt that the enlargement of the work has rendered it advisable for him to confine his additions to the narrowest compass. In the portion devoted to Organic Chemistry, the very recent revision by Mr. Watts has presented so complete a view of the most modern aspect of the subject that there has been nothing to add. In the earlier portion, however, some few discoveries, announced since its publication, a year ago, have been introduced. For the convenience of students who are not familiar with the Decimal System of weights and measures, and the Centigrade thermometer, the corresponding figures of the standards in popular use have been introduced in brackets. This will afford a means of comparison, by attention to which the reader can readily accustom himself to the metric system, which is so rapidly superseding all others in scientific investigation.

In its enlarged and improved shape it is hoped that the work will fully maintain its claim to the favor which it has so long enjoyed as a full and intelligible guide to Chemical Science.

PHILADELPHIA, May, 1878.



PREFACE.

THE design of this work is to offer to the student commencing the study of Chemistry an outline of the general principles of that science, and a history of the more important among the very numerous bodies which Chemical Investigations have made known to us. It has no pretensions to be considered a complete treatise on the subject, but is intended to serve as an introduction to the larger and more comprehensive systematic works in our own language and in those of the Continent; and especially to prepare the student for the perusal of original memoirs, which, in conjunction with practical instruction in the laboratory, can alone afford a real acquaintance with the spirit of research and the resources of Chemical Science.

The first three editions were prepared by the Author, the third being nearly completed shortly before his death in January, 1849, and published at the beginning of the following year, under the editorship of his friend, the late Dr. H. Bence Jones.

In the six following editions, which were edited by Dr. Bence Jones and Dr. Hofmann, a large amount of new and important matter was added; and in the tenth edition (1868), by Dr. Bence Jones and the present Editor, it was found necessary, in consequence of the rapid advance of the science, and the great changes which had taken place in the entire system of Chemical Philosophy, to make considerable alterations and additions in almost every part of the work.

The chapter on the General Principles of Chemical Philosophy was accordingly re-written; considerable additions were made to the descriptions of the metals, especially those of rarer occurrence; and the distinguishing reactions of the several metals were given more fully than in former editions. The greater part of the Organic Chemistry was also re-written,

especially the sections relating to the Hydrocarbons, Alcohols, and Acids, and the compounds belonging to each of these groups were arranged in series.

In the last edition, a considerable amount of new matter was added, chiefly relating to Organic Chemistry; and as these additions are continually increasing, it has been found necessary, in the present edition, to divide the work into two volumes, the first including Chemical Physics and Inorganic Chemistry, and the second being devoted to Organic Chemistry.

The plan adopted by the Author, of describing the non-metallic elements and their compounds with one another, before entering upon the discussion of the general principles of Chemical Philosophy, is retained, as the understanding of these General Principles is greatly facilitated by the previous study of a number of special instances of their application; but a short statement of the most important Laws of Chemical Combination, and of the fundamental principles of the Atomic Theory, is given immediately after the description of the compounds of oxygen, in order to introduce the student as soon as possible to the expression of chemical combinations and reactions by Symbolic Notation.

The Weights and Measures used are those of the French Decimal System. Temperatures are expressed in the Centigrade Scale, except where the contrary is stated. A comparative Table of the Centigrade and Fahrenheit Scales is given at the end of the first volume.

LONDON, February, 1877.

The division of this Manual into two volumes has afforded the means of treating the subject of ORGANIC CHEMISTRY more fully than was possible in the previous Editions.

The arrangement adopted in the present Edition is the same in principle as in the last, organic compounds being classified according to their chemical structure and functions—as Hydrocarbons, Alcohols, Ethers, Acids, Bases, etc., and the compounds in each group arranged in Homologous Series.

Particular attention has been given to the study of Isome-

ri sm, especially amongst the Derivatives of Benzene, our knowledge of the isomeric relations of these bodies having lately attained—through the classical researches of Koerner and other distinguished chemists—a high degree of precision and completeness. This part of the subject is here presented in a form in which it has not yet appeared in any English publication, except the “Journal of the Chemical Society.”

The portion of the previous Editions relating to Physiological Chemistry—including the description of the Tissues and Fluids of the Animal Body, and the Functions of Nutrition and Respiration—is omitted in the present Edition, this department of Chemistry having now become so extensive as to require treatment in separate works.

HENRY WATTS.

September, 1877.



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A

MANUAL OF CHEMISTRY.

INTRODUCTION.

THE Science of Chemistry has for its object the study of the nature and properties of all the materials which enter into the composition or structure of the earth, the sea, and the air, and of the various organized or living beings which inhabit them. Every object accessible to man is thus embraced by the wide circle of Chemical Science.

In ordinary scientific speech the term *chemical* is applied to changes which permanently affect the properties or characters of bodies, in opposition to effects termed *physical*, which are not attended by such consequences. Changes of decomposition or combination are thus easily distinguished from those temporarily brought about by heat, electricity, magnetism, and the attractive forces, whose laws and effects lie within the province of Physics or Natural Philosophy.

Nearly all the objects presented by the visible world are of a compound nature, being chemical compounds, or variously disposed mixtures of chemical compounds, capable of being resolved into simpler forms of matter. Thus, a piece of limestone or marble, by the application of a red heat, is decomposed into quicklime and a gaseous body, carbon dioxide. Both lime and carbon dioxide are in their turn susceptible of decomposition, the former into calcium and oxygen, the latter into carbon and oxygen. For this purpose, however, simple heat does not suffice, the resolution of these substances into their components demanding the exertion of a high degree of chemical energy. Beyond this second step of decomposition the efforts of Chemistry have hitherto been found to fail; and the three bodies, calcium, carbon, and oxygen, having resisted all attempts to resolve them into simpler forms of matter, are accordingly admitted into the list of *elements*; not from an absolute belief in their real oneness of nature, but from the absence of any evidence that they contain more than one description of matter.

The elementary bodies, at present recognized, are sixty-four in number, and about fifty of them belong to the class of *metals*. Several of these are

of recent discovery, and are as yet very imperfectly known. The distinction between metals and non-metallic substances, although very convenient for purposes of description, is entirely arbitrary, since the two classes graduate into each other in the most complete manner.

The names of the elements are given in the following table. Opposite to them in the third column are placed certain numbers, which express the proportions in which they combine together, or simple multiples of those proportions; these numbers, for reasons which will be afterwards explained, are called Atomic or Indivisible Weights. In the second column are placed symbols by which these weights are denoted; these symbols are formed of the first letters of the Latin names of the elements, a second letter being added when the names of two or more elements begin with the same letter.

The names of the most important elements are distinguished by the largest and most conspicuous type; those next in importance, by small capitals; while the names of elements which are of rare occurrence, or of which our knowledge is still imperfect, are printed in the ordinary type. The names with an asterisk are those of Non-metallic Elements, the others are names of Metals.

It must be distinctly understood that the atomic or combining weights assigned to the elements are merely relative. The number 1 assigned to hydrogen may represent a grain, ounce, pound, gram, kilogram, etc., and the numbers assigned to the other elements will then represent so many grains, ounces, pounds, grams, kilograms, etc. Hydrogen is taken as the unit of the scale, because its combining weight is smaller than that of any other element; but this is merely a matter of convenience; in the older tables of atomic weights that of oxygen was assumed as 100, that of carbon being then 75, that of hydrogen 6.25, etc. etc.

TABLE OF ELEMENTARY BODIES, WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

| Name. | Symbol. | Atomic Weight. | Name. | Symbol. | Atomic Weight. |
|------------------------------------|---------|----------------|--------------------------------|---------|----------------|
| ALUMINIUM | Al | 27.4 | Molybdenum | Mo | 96 |
| ANTIMONY (Stibium) | Sb | 122 | NICKEL | Ni | 58.8 |
| ARSENIC | As | 75 | Niobium | Nb | 94 |
| BARIUM | Ba | 137 | NITROGEN* | N | 14 |
| BERYLLIUM | Be | 9.4 | Osmium | Os | 199.2 |
| BISMUTH | Bi | 210 | OXYGEN* | O | 16 |
| BORON* | B | 11 | PALLADIUM | Pd | 106.6 |
| BROMINE* | Br | 80 | PHOSPHORUS* | P | 31 |
| Cadmium | Cd | 112 | PLATINUM | Pt | 197.4 |
| Cesium | Cs | 133 | POTASSIUM | | |
| CALCIUM | Ca | 40 | (Kalium) | K | 39.1 |
| CARBON* | C | 12 | Rhodium | Rh | 104.4 |
| Cerium | Ce | 92 | Rubidium | Rb | 85.4 |
| CHLORINE* | Cl | 35.5 | Ruthenium | Ru | 104.4 |
| Chromium | Cr | 52 | Selenium* | Se | 79.4 |
| COBALT | Co | 58.8 | SILICIUM* | Si | 28 |
| COPPER (Cu-
prum) | Cu | 63.4 | SILVER (Argen-
tum) | Ag | 108 |
| Dysprosium | D | 95 | SODIUM (Na-
trium) | Na | 23 |
| Erbium | E | 168.9 | STRONTIUM | Sr | 87.6 |
| FLUORINE* | F | 19 | S | S | 32 |
| Gadolinium | Ga | 68.7 | SULPHUR* | | |
| GOLD (Aurum) | Au | 197 | Tantalum | Ta | 182 |
| HYDROGEN* | H | 1 | Tellurium* | Te | 128 |
| Indium | In | 113.4 | Thallium | Tl | 204 |
| IODINE* | I | 127 | Thorium | Th | 235 |
| Iridium | Ir | 198 | TIN (Stannum) | Sn | 118 |
| IRON (Ferrum) | Fe | 56 | Titanium | Ti | 50 |
| Lanthanum | La | 91.8 | TUNGSTEN, or Wolf-
ram | W | 184 |
| LEAD (Plumbum) | Pb | 207 | URANIUM | U | 240 |
| Lithium | Li | 7 | Vanadium | V | 51.2 |
| Magnesium | Mg | 24 | Yttrium | Y | 92 |
| MANGANESE | Mn | 55 | ZINC | Zn | 65.2 |
| MERCURY (Hy-
drargyrum) | Hg | 200 | Zirconium | Zr | 89.6 |

By the combination of the elements in various proportions, and in groups of two, three, or larger numbers, all known compound bodies are produced. And here it is important to state clearly the characters which distinguish true chemical combination from mechanical mixture, and from that kind of adhesion which gives rise to the solution of a solid in a liquid. Bodies may be mixed together in any proportion whatever, the mixture always exhibiting properties intermediate between those of its constituents, and in regular gradation, according to the quantity of each that may be present, as may be seen in the fusion together of metals to form alloys, in the mixture of water with alcohol, of alcohol with ether, and of different oils one with the other. A solid body may also be dissolved in a liquid—salt or sugar

in water, for example—in any proportion up to a certain limit, the solution likewise exhibiting a regular gradation of physical properties, according to the quantity of the solid taken up. But a true chemical compound exhibits properties totally different from those of either of its constituent elements, and the proportion of these constituents which form that particular compound admits of no variation whatever. Water, for example, is composed of two elements, oxygen and hydrogen, which, when separated from one another, appear as colorless gases, differing widely in their properties one from the other, and from water in the state of vapor; moreover, water, whether obtained from natural sources, or formed by direct combination of its elements, always contains in 100 parts by weight, 88.9 parts of oxygen and 11.1 of hydrogen. Common salt, to take another example, is a compound of chlorine and sodium, the former of which, in the separate state, is a yellow gas, the latter a yellowish-white highly lustrous metal, capable of burning in the air, and decomposing water; moreover, from whatever part of the world the salt may be obtained, 100 parts of it invariably contain 39.6 parts of sodium and 60.4 parts of chlorine. Further, when two or more compounds are formed of the same elements, there is no gradual blending of one into the other, as in the case of mixtures, but each compound is sharply defined, and separated, as it were, from the others by an impassable gulf, exhibiting properties distinct from those of the others, and of the elements themselves in the separate state. Thus, there are two compounds of carbon and oxygen, one of which, containing 3 parts by weight of carbon with 4 of oxygen, is an inflammable gas, lighter than atmospheric air, and not absorbed by solution of potash; while the other, which contains 3 parts of carbon and 8 of oxygen, is non-inflammable, heavier than air, and easily absorbed by potash.

Before proceeding with the special description of the several elements and their compounds, it will be convenient to give a short sketch of certain branches of Physical Science, as the physical constitution of Gases, and the chief phenomena of Heat, Light, and Electricity, the partial study of which forms indeed an indispensable Introduction to Chemistry.

PART I.—PHYSICS.

OF DENSITY AND SPECIFIC GRAVITY.

It is of great importance at the outset to understand clearly what is meant by the terms *density* and *specific gravity*. By the *density* of a body is meant its *mass*, or *quantity of matter*, compared with the mass or quantity of matter of an *equal volume* of some standard body, arbitrarily chosen. *Specific gravity* denotes the weight of a body, as compared with the weight of an equal bulk, or volume, of the standard body, which is reckoned as unity.* In all cases of solids and liquids the standard of unity adopted in this country is pure water at the temperature of 15.5° C. (60° Fahr.). Anything else might have been chosen; there is nothing in water to render its adoption for the purpose mentioned indispensable: it is simply taken for the sake of convenience, being always at hand, and easily obtained in a state of perfect purity. An ordinary expression of specific weight, therefore, is a number expressing how many times the weight of an equal bulk of water is contained in the weight of the substance spoken of. If, for example, we say that concentrated oil of vitriol has a specific gravity equal to 1.85, or that perfectly pure alcohol has a density of 0.794 at 15.5° C., we mean that equal bulks of these two liquids and of distilled water possess weights in the proportion of the numbers 1.85, 0.794, and 1; or 1850, 794, and 1000. It is necessary to be particular about the temperature, for, as will be hereafter shown, liquids are extremely expansible by heat; otherwise a constant bulk of the same liquid will not retain a constant weight. It will be proper to begin with the description of the mode in which the specific gravity of liquids is determined: this is the simplest case, and the one which best illustrates the general principle.

To find the specific gravity of any particular liquid compared with that of water, it is only requisite to weigh equal bulks at the standard temperature, and then divide the weight of the liquid by the weight of the water; the quotient will be greater or less than unity, as the liquid experimented on is heavier or lighter than water. Now, to weigh equal bulks of two fluids, the simplest and best method is clearly to weigh them in succession in the same vessel, taking care that it is equally full on both occasions.

A thin glass bottle, or flask, with a narrow neck, is procured, of the form represented on the next page (fig. 1), and of such capacity as to contain, when filled to about half-way up the neck, exactly 1000 grains of distilled water at 15.5° C. A counterpoise of the exact weight of the empty bottle is made from a bit of brass, an old weight, or something of the kind, and carefully adjusted by filing. The bottle is then graduated, by introducing water

* In other words, density means comparative mass, and specific gravity comparative weight. These expressions, although really relating to distinct things, are often used quite indifferently in chemical writings, and without practical inaccuracy, since mass and weight are directly proportional to each other.

at 15.5° , until it exactly balances the 1000-grain weight and counterpoise in the opposite scale; the height at which the water stands in the neck is marked by a scratch, and the instrument is complete for use. The liquid to be examined is brought to the temperature of 15.5° , and with it the bottle is filled up to the mark before mentioned; it is then weighed, the counterpoise being used as before, and the specific gravity directly ascertained.

Fig. 1.



Fig. 2.



A watery liquid in a narrow glass tube always presents a curved surface, from the molecular action of the glass, the concavity being upwards. It is better, on this account, in graduating the bottle, to make two scratches, as represented in the figure, one at the top and the other at the bottom of the curve. The marks are easily made by a fine, sharp, triangular file, the hard point of which, also, it may be observed, answers perfectly well for writing upon glass, in the absence of a diamond pencil.

It will be quite obvious that the adoption of a flask holding exactly 1000 grains of water has no other object than to save the trouble of a very trifling calculation; any other quantity would answer just as well, and, in fact, the experimental chemist is often compelled to use a bottle of much smaller dimensions, from scarcity of the liquid to be examined.

When the specific gravity of a liquid is to be determined with great accuracy, a case which frequently occurs in chemical inquiries, a little glass bottle is used, of the form shown in fig. 2. This bottle is provided with a perforated conical glass stopper, most accurately fitted by grinding. By completely filling the bottle with liquid, and carefully removing the portion of liquid which is displaced when the stopper is inserted, an unalterable measure is obtained. The least possible quantity of grease applied to the stopper greatly promotes the exact fitting.

When the chemist has only a very small quantity of a fluid at his disposal, and wishes not to lose it, the little glass vessel (fig. 3) is particu-

very useful. It is formed by blowing a bulb on a glass tube, on that portion of the tube which is narrowed by drawing the tube out over a lamp, a fine scratch is made with a diamond. The bulb is filled up to this mark with the liquid whilst it floats in water, the temperature of which is exactly known. A very fine funnel is used for filling the bulb, the stem of the funnel being drawn out so as to enter the tube, and the upper opening of the funnel being small enough to be closed by the finger. The glass stopper is only wanted as a guard, and does not require to fit perfectly.

The determination of the specific gravity of a solid body is made according to the same principles, and may be performed with the specific-gravity bottle (fig. 2). The bottle is first weighed full of water; the solid is then placed in the same pan of the balance, and its weight is determined; finally, the solid is put into the bottle, displacing an equal bulk of water, the weight of which is determined by the loss on again weighing. Thus the weights of the solid and that of an equal bulk of water are obtained. The former divided by the latter gives the specific gravity.



| | |
|--|---------------|
| For example, the weight of a small piece of silver wire was found to be | 98.18 grains. |
| Glass bottle filled with water | 294.69 " |
| | <hr/> |
| | 392.87 " |
| After an equal volume of water was displaced by the silver, the weight was | 383.54 " |
| | <hr/> |
| Hence the displaced water weighed | 9.33 " |
| From this the specific gravity of the silver wire } 98.18 | |
| is } 9.33 | = 10.523 " |

Another highly ingenious, but less exact method of determining the specific gravity of solids, is based on the well-known theorem of Archimedes.

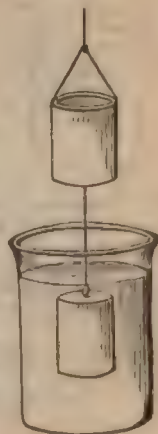
This theorem may be thus expressed:—

When a solid is immersed in a fluid, it loses a portion of its weight; and this portion is equal to the weight of the fluid which it displaces; that is, to the weight of its own bulk of that fluid.

Fig. 4.

It is easy to give experimental proof of this very important proposition, as well as to establish it by reasoning. Figure 4 represents a little apparatus for the former purpose. This consists of a thin cylindrical vessel of brass, into the interior of which fits very accurately a solid cylinder of the same metal, thus nearly filling it. When the cylinder is suspended beneath the bucket, as seen in the sketch, the whole hangs from the arm of a balance and counterpoised, and then the cylinder itself immersed in water, it will be found to have lost a certain weight; and that this loss is precisely equal to the weight of an equal bulk of water may then be proved by filling the bucket to the brim, whereupon the equilibrium will be restored.

The consideration of the great hydrostatic law of fluid pressure easily proves the truth of the principle



laid down. Let the reader figure to himself a vessel of water, having immersed in it a solid cylindrical or rectangular body, and so adjusted with respect to density, that it shall float indifferently in any part beneath the surface (fig. 5).

Fig. 5.



Now the law of fluid pressure is to this effect:—

The pressure exerted by a fluid on any point of the containing vessel, or on any point of a body immersed beneath its surface, is dependent, firstly, upon the density of the fluid, and, secondly, upon the vertical depth of the point in question below the surface. It is independent of the form and lateral dimensions of the vessel or immersed body. Moreover, owing to the peculiar physical constitution of fluids, this pressure is exerted in every direction, upwards, downwards, and laterally, with equal force.

The floating body is in a state of equilibrium; therefore the pressure downwards caused by its gravitation must be exactly compensated by the upward transmitted pressure of the column of water, *a, b*. But this pressure downwards is obviously equal to the weight of an equal quantity of water, since the body of necessity displaces its own bulk. Hence, the weight which a body loses when immersed in, or floated on water, is equal to the weight of the volume of water displaced by that body.

Whatever be the density of the substance, it will be buoyed up to this amount; in the case supposed, the buoyancy is equal to the whole weight of the body, which is thus, while in the water, reduced to nothing.

Fig. 6.



A little reflection will show that the same reasoning may be applied to a body of irregular form; besides, a solid of any figure may be divided by the imagination into a multitude of little perpendicular prisms or cylinders, to each of which the argument may be applied. What is true of each individually must necessarily be true of the whole together.

This is the fundamental principle; its application is made in the following manner: Let it be required, for example, to know the specific gravity of a body of extremely irregular form, as a small group of rock crystals: the first part of the operation consists in determining its absolute weight, or, more correctly speaking, its weight in air; it is next suspended from the balance-pan by a fine horsehair, immersed completely in pure water at 15.5° , and again weighed. It now weighs less, the difference being the weight of the water it displaces, that is, the weight of an equal bulk. This being known, nothing more is required than to find,

by division, how many times the latter number is contained in the former; the quotient will be the density, water at the temperature of 15.5° being taken = 1. For example:—

| | | | | | |
|--|---|---|---|---|---------------|
| The quartz-crystals weigh in air | . | . | . | . | 293.7 grains. |
| When immersed in water, they weigh | . | . | . | . | 180.1 " |
| Difference, being the weight of an equal volume of water | | | | | 113.6 " |

$$\frac{293.7}{113.6} = 2.59, \text{ the specific gravity required.}$$

The rule is generally thus written: "Divide the weight in air by the weight in water, and the quotient will be the specific gravity." In reality it is not the weight in air which is required, but the weight the body would have in empty space: the error introduced, namely, the weight of an equal bulk of air, is so small that it is usually neglected.

Fig. 7.



Sometimes the body to be examined is lighter than water, and floats. In this case, it is first weighed, and afterwards attached to a piece of metal heavy enough to sink it, and suspended from the balance. The whole is then exactly weighed, immersed in water, and again weighed. The difference between the two weighings gives the weight of a quantity of water equal in bulk to both together. The light substance is then detached, and the same operation of weighing in air, and again in water, repeated on the piece of metal. These data give the means of finding the specific gravity, as will be at once seen by the following example:—

| | |
|--|---------------|
| Light substance (a piece of wax) weighs in air | 133.7 grains. |
| Attached to a piece of brass, the whole now weighs | 183.7 " |
| Immersed in water, the system weighs | 38.8 " |
| Weight of water equal in bulk to brass and wax | 144.9 " |
| Weight of brass in air | 50.0 " |
| Weight of brass in water | 44.4 " |
| Weight of equal bulk of water | 5.6 " |
| Bulk of water equal to wax and brass | 144.9 " |
| Bulk of water equal to brass alone | 5.6 " |
| Bulk of water equal to wax alone | 139.3 " |

$$\frac{133.7}{139.3} = 0.9598.$$

In all such experiments, it is necessary to pay attention to the temperature and purity of the water, and to remove with great care all adhering air-bubbles;* otherwise, a false result will be obtained.

Other cases require mention in which these operations must be modified to meet particular difficulties. One of these happens when the substance to be weighed or acted upon by water. The difficulty is easily overcome by substituting some other liquid of known density which experience shows is without action. Alcohol or oil of turpentine may generally be used when water is inadmissible. Suppose, for instance, the specific gravity of crystallized sugar is required, we proceed in the following way: The specific gravity of the oil of turpentine is first carefully determined; let it be 0.85, the sugar is next weighed in the air, then suspended by a horse-hair, and weighed in the oil; the difference is the weight of an equal bulk

* A simple plan of avoiding altogether the adhesion of air-bubbles, which often are not easily perceived, consists in heating the water to ebullition, introducing the body which has been weighed in the air into the still boiling water, which is then allowed to cool to 15.5°, when the second weighing is performed.

of the latter; a simple calculation gives the weight of a corresponding volume of water:—

| | |
|---|-------------|
| Weight of sugar in air | 400 grains. |
| Weight of sugar in oil of turpentine | 182.5 " |
| <hr/> | |
| Weight of equal bulk of oil of turpentine | 217.5 " |
| <hr/> | |
| 87 : 100 = 217.5 : 250, | |

the weight of an equal bulk of water; hence the specific gravity of the sugar—

$$\frac{400}{250} = 1.6.$$

If the substance to be examined consists of small pieces, or of powder, the method first described, namely, that of the specific gravity bottle, can alone be used.

By this method the specific gravities of metals in powder, metallic oxides, and other compounds, and salts of all descriptions, may be determined with great ease. Oil of turpentine may be used with most soluble salts. The crystals should be crushed or roughly powdered, to avoid errors arising from cavities in their substance.

The specific gravity of a solid can also be readily found by immersing it in a transparent liquid, the density of which has been so adjusted that the solid body remains indifferently at whatever depth it may be placed. The specific gravity of the liquid must now be determined, and it will, of course, be the same as that of the solid. It is necessary that the liquid chosen for this experiment do not dissolve or in any way act upon the solid. Solutions of mercuric nitrate, or corrosive sublimate, can be used for bodies heavier than water, whilst certain oils, and essences, and mixtures of alcohol and water, can be conveniently employed for such substances as have a lower specific gravity than water. This method is not only adapted to the exact determination of specific gravities, but also serves, in many cases, as a means of readily distinguishing substances much resembling one another. Suppose, for instance, a solution of mercuric nitrate to have a specific gravity 3; a red amethyst (2.67) will then float upon, and a topaz of the same color (3.55) will sink in this liquid.

Hydrometers.—The theorem of Archimedes affords the key to the general doctrine of the equilibrium of floating bodies, of which an application is made in the common hydrometer,—an instrument for finding the specific gravities of liquids in a very easy and expeditious manner.*

When a solid body is placed upon the surface of a liquid specifically

* The mode of determining the specific gravity of a liquid by means of a solid has been omitted in the text. It results from the theorem of Archimedes, that if any solid be immersed in water and then in any other liquid, the loss of weight sustained in each case will give the relative weights of equal bulks of the liquids, and on dividing the weight of the liquid by the weight of the water, the quotient will be the specific gravity of the liquid experimented on. For instance, let a piece of glass rod be suspended from the balance-pan and exactly counterpoised, then immerse it in water and restore the equilibrium by weights added to the pan to which the glass is suspended, the amount will give the loss of weight by immersion or the weight of a bulk of water equal to that of the rod. Now wipe the glass dry, and having removed the additional weights, immerse it in the other liquid, and restore the equilibrium as before; this latter weight is the weight of a bulk of the liquid equal to that of the water. The latter divided by the former gives the specific gravity. For example:—

| | |
|---|-------------|
| The glass rod loses by immersion in water | 171 grains. |
| The glass rod loses by immersion in alcohol | 143 |

$$\frac{143}{171} = .830, \text{ the specific gravity required.} \text{—R.B.}$$

Fig. 8.



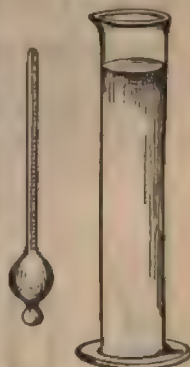
heavier than itself, it sinks down until it displaces a quantity of liquid equal to its own weight, at which point it floats. Thus, in the case of a substance floating in water, whose specific weight is one-half that of the liquid, the position of equilibrium will involve the immersion of exactly one-half of the body, inasmuch as its whole weight is counterpoised by a quantity of water equal to half its volume. If the same body were put into a liquid of one-half the specific gravity of water, if such could be found, it would then sink beneath the surface, and remain indifferently in any part. A floating body of known specific gravity may thus be used as an indicator of the specific gravity of a liquid. In this manner little glass beads (fig. 9) of known specific gravities are sometimes employed in the arts to ascertain in a rude manner the specific gravity of liquids; the one that floats indifferently beneath the surface, without either sinking or rising, has of course the same specific gravity as the liquid itself; this is pointed out by the number marked upon the bead.

Fig. 9.



The hydrometer (fig. 10) in general use consists of a floating vessel of thin metal or glass, having a weight beneath to maintain it in an upright position and a stem above bearing a divided scale. The use of the instrument is very simple. The liquid to be tried is put into a small narrow jar, and the instrument floated in it. It is obvious that the denser the liquid, the higher will the hydrometer float, because a smaller displacement of liquid will counterbalance its weight. For the same reason, in a liquid of less density, it sinks deeper. The hydrometer comes to rest almost immediately, and then the mark on the stem at the last level may be read off.

Fig. 10.



Very extensive use is made of instruments of this kind in the arts: they sometimes bear different names, according to the kind of liquid for which they are intended; but the principle is the same in all. The graduation is very commonly arbitrary, two or three different scales being unfortunately used. These may be sometimes reduced, however, to the true numbers expressing the specific gravity by the aid of tables of comparison drawn up for the purpose. (See APPENDIX.) Tables are likewise used to reduce the readings of the hydrometer at any temperature to those of the normal temperature.

It is much better, however, to use a hydrometer having the true scale of specific gravities marked upon its stem. To graduate such an instrument a sufficient number of standard points may be determined by immersing it in liquids of known specific gravity, and the small intervals between these points divided into equal parts.*

The determination of the specific gravity of gases and vapors of volatile liquids is a problem of very great practical importance to the chemist: the theory of the operation is as simple as when liquids themselves are concerned, but the processes are much more delicate, and involve besides certain corrections for differences of temperature and pressure, founded on principles yet to be discussed. It will be proper to defer the consideration of these matters for the present.

* For an accurate method of dividing the hydrometer scale when only a few points are determined by actual observation, see the article "Hydrometer," by Professor Jerrard, in *Watts's Dictionary of Chemistry*, vol. iii. p. 209.

THE PHYSICAL CONSTITUTION OF THE ATMOSPHERE AND OF GASES IN GENERAL.

It requires some little abstraction of mind to realize completely the condition in which all things at the surface of the earth exist. We live at the bottom of an immense ocean of gaseous matter, which envelops everything, and presses upon everything with a force which appears, at first sight, perfectly incredible, but whose actual amount admits of easy proof.

Gravity being, so far as is known, common to all matter, it is natural to expect that gases, being material substances, should be acted upon by the earth's attraction, as well as solids and liquids. This is really the case, and the result is the weight or pressure of the atmosphere, which is nothing more than the effect of the attraction of the earth on the particles of air.

Before describing the leading phenomena of the atmospheric pressure, it is necessary to notice one very remarkable feature in the physical constitution of gases, upon which depends the principle of the air-pump.

Gases are in the highest degree elastic; the volume or space which a gas occupies depends upon the pressure exerted upon it.

Fig. 11.



Let the reader imagine a cylinder, *a*, closed at the bottom, in which moves a piston air-tight, so that no air can escape between the piston and the cylinder. Suppose now the piston be pressed downwards with a certain force; the air beneath it will be compressed into a smaller bulk, the amount of this compression depending on the force applied; if the power be sufficient, the bulk of the gas may be thus diminished to one-hundredth part or less. When the pressure is removed, the elasticity or *tension*, as it is called, of the included air or gas, will immediately force up the piston until it arrives at its first position.

Again, take Fig. 11, *b*, and suppose the piston to stand about the middle of the cylinder, having air beneath in its usual state. If the piston be now drawn upwards, the air below will expand, so as to fill completely the increased space, and this to an apparently un-

limited extent. A volume of air which, under ordinary circumstances, occupies the bulk of a cubic inch, might, by the removal of the pressure upon it, be made to expand to the capacity of a whole room, while a renewal of the former pressure would be attended by a shrinking down of the air to its former bulk. The smallest portion of gas introduced into a large exhausted vessel becomes at once diffused through the whole space, an equal quantity being present in every part; the vessel is *full*, although the gas is in a state of extreme tenuity. This power of expansion which air possesses may have, and probably has, in reality, a limit; but the limit is never reached in practice. We are quite safe in the assumption that, for all purposes of experiment, however refined, air is perfectly elastic.

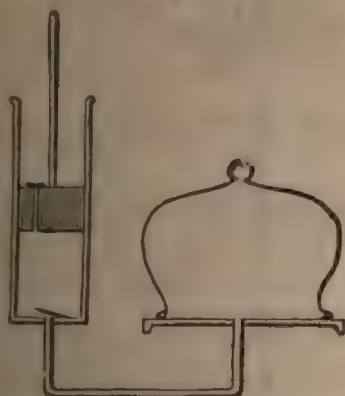
usual to assign a reason for this indefinite expansibility by ascribing particles of material bodies, when in a gaseous state, a self-repulsive

The statement is commonly made somewhat in this manner:—
 is under the influence of two opposite forces, one of which tends to
 the particles together, the other to separate them. By the preponderance
 of one or other of these forces, we have the three states called solid,
 and gaseous. When the particles of matter, in consequence of the
 and strength of their mutual attractions, possess only a very
 power of motion, a solid substance results; when the forces are
 balanced, we have a liquid, the particles of which in the interior
 mass are free to move, but yet, to a certain extent, are held together;
 only, when the attractive power seems to be completely overcome by
 repulsion, we have a gas or vapor.

These names are applied to these forces, and various ideas entertained
 among them: the attractive forces bear the name of cohesion when
 is exerted between particles of matter separated by an immeasurably
 interval, and gravitation when the distance is great. The repul-
 sion often appears to be identical with the principle of heat. We shall
 on this subject in discussing the dynamical theory of heat.

Air-Pump.—The ordinary air-pump, shown in section in fig. 12,
 is essentially of a metallic cylinder, in which moves a tightly-fitting
 by the aid of its rod. The bottom of the cylinder communicates
 the vessel to be exhausted, and is furnished with a valve opening
 outwards. A similar valve, also opening upwards, is fitted to the piston;
 valves are made with slips of oiled silk. When the piston is raised

Fig. 12.



bottom of the cylinder, the space left beneath it must be void of
 the piston-valve opens only in one direction; the air within the
 having on that side nothing to oppose its elastic power but the
 of the little valve, lifts the latter, and escapes into the cylinder.
 As the piston begins to descend, the lower valve closes, by its own
 or by the pressure transmitted from above, and communication
 the receiver is cut off. As the descent of the piston continues, the
 of air in the cylinder becomes compressed, its elasticity is increased,
 length it forces open the upper valve, and escapes into the atmos-

phere. In this manner, a cylinder full of air is removed from the receiver at every stroke of the pump. During the descent of the piston, the upper valve remains open, and the lower closed, and the reverse during the opposite movement.

In practice, it is very convenient to have two such barrels or cylinders, arranged side by side, the piston-rods of which are formed into racks, having a pinion or small-toothed wheel between them, moved by a winch.

Fig. 13.

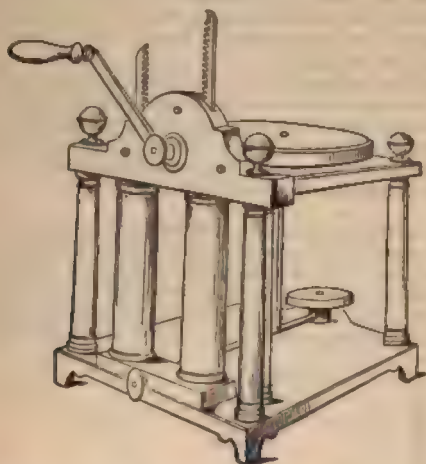
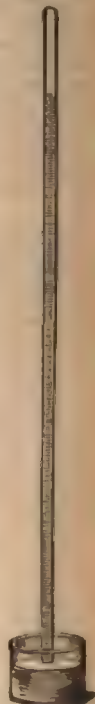


Fig. 14.



By this contrivance the operation of exhaustion is much facilitated, and the labor lessened. The arrangement is shown in fig. 13.

Atmospheric Pressure—The Barometer.—Air has weight; a light flask or globe of glass, furnished with a stop-cock and exhausted by the air-pump, weighs considerably less than when full of air. If the capacity of the vessel be equal to 100 cubic inches, the difference may amount to nearly 30 grains.

After what has been said on the subject of fluid pressure, it will scarcely be necessary to observe that the law of equality of pressure in all directions also holds good in the case of the atmosphere. The perfect mobility of the particles of air permits the transmission of the force generated by their gravity. The sides and bottom of an exhausted vessel are pressed upon with as much force as the top.

If a glass tube of considerable length could be perfectly exhausted of air, and then held in an upright position, with one of its ends dipping into a vessel of liquid, the latter, on being allowed access to the tube, would rise in its interior until the weight of the column balanced the pressure of the air upon the surface of the liquid. Now, if the density of this liquid were known, and the height and area of the column measured, means would be furnished for exactly estimating the amount of pressure exerted by the atmosphere. Such an instrument is the barometer. To construct

A straight glass tube, 36 inches long, is sealed by the blowpipe flame at the top; it is then filled with clean, dry mercury, care being taken to exclude all air-bubbles, the open end stopped with a finger, and the tube held in a basin of mercury. On removing the finger, the mercury falls from the top of the tube, until it stands at the height of about 30 inches above the level of that in the basin. Here it remains supported by, balancing the atmospheric pressure, the space above the mercury in the tube being of necessity empty.

The pressure of the atmosphere is thus seen to be capable of sustaining a column of mercury 30 inches in height, or thereabouts. Now such a column, having an area of 1 inch, weighs between 14 and 15 lbs.; consequently such must be the amount of the pressure exerted upon every square inch of the surface of the earth, and of the objects situated thereon, at least at the level of the sea. This enormous force is borne without inconvenience by the animal frame, by reason of its perfect uniformity in every direction; and it may be doubled, or even tripled, without injury.

A barometer may be constructed with other liquids besides mercury; but, as the height of the column must always bear an inverse proportion to the density of the fluid, the length of tube required will be often considerable; in the case of water it will exceed 34 feet.

It is seldom that any other liquid than mercury is employed in the construction of this instrument.

The Royal Society of London possessed a water barometer in its apartments at Somerset House.

Its construction was attended with great difficulties, and it was found impossible to keep it free from air.

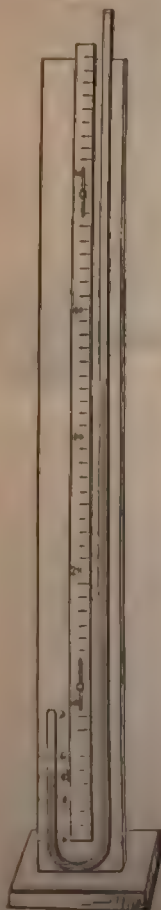
Sprengel's Air-Pump.—If an aperture be made in the top of the barometer tube the mercury will sink, and draw in air; and the experiment be so arranged that air may be allowed to enter along the tube, and the supply of air is limited, while that of mercury is unlimited, the air may be carried away and vacuum produced. On this principle, Dr. Sprengel has constructed an apparatus by which a complete exhaustion may be effected. (Fig. 15) is a glass tube longer than a barometer, sealed at both ends, and connected, by means of India-rubber tubing, to a funnel A filled with mercury and supported on a stand. The funnel is allowed to fall through a stopper at a rate regulated by a screw at c; the lower end of the

Fig. 15.



tube *cd* fits into the flask B, which has a spout at its side, a little higher than the lower end of the tube *cd*; the upper part of this tube has a branch at *x*, to which a receiver R can be tightly fixed. When the clamp at *c* is opened, the first portion of mercury that runs out closes the tube and prevents air from entering below. As the mercury is allowed to run down, the exhaustion begins, and the whole length of the tube from *x* to *d* is filled with cylinders of air and mercury having a downward motion. Air and mercury escape through the spout of the bulb B, below which is placed a basin H to receive the mercury; and this mercury is poured back from time to time into the funnel A, to be repassed through the tube till the exhaustion is complete. As this point is approached, the

Fig. 16.



inclosed air between the mercury cylinders is seen to diminish, until the lower part of *cd* forms a continuous column of mercury about 30 inches high. The operation is complete when the column of mercury is quite free from air, and a drop of mercury falls on the top of it without inclosing the smallest air-bubble. The height of the column is then equal to that of the mercury in the barometer; in other words, the apparatus is a barometer whose vacuum is the receiver R. It may be advantageously combined with an exhausting syringe, which removes the greater part of the air, the exhaustion being then completed as above.

Relations between Pressure, Elasticity, and Volume of Gases.—It will now be necessary to consider a most important law which connects the volume occupied by a gas with the pressure made upon it, and is thus expressed:—

The volume of gas is *inversely* as the pressure; the density and elastic force are *directly* as the pressure, and *inversely* as the volume.

For instance, 100 cubic inches of gas under a pressure of 30 inches of mercury would expand to 200 cubic inches were the pressure reduced to one-half, and shrink, on the contrary, to 50 cubic inches if the original pressure were doubled. The change of density must necessarily be in the inverse proportion to that of the volume, and the elastic force follows the same rule.

This, which is usually called the law of Mariotte, though really discovered by Boyle (1661), is easily demonstrable by direct experiment. A glass tube (fig. 16), about 7 feet long, is closed at one end, and bent into the form represented in fig. 16, the open limb of the syphon being the longer. It is next attached to a board furnished with a movable scale of inches, and enough mercury is introduced to fill the bend, the level being evenly adjusted and marked upon the board. Mercury is now poured into the tube until the inclosed air is reduced to one half of its former volume; and on applying the scale, it will be found that the level of the mercury in the open part of the tube stands very nearly 30 inches above that in the closed portion. The pressure of an additional "atmosphere" has consequently reduced the bulk of the contained air to one-half. If the experi-

ment be still continued until the volume of air is reduced to a third, it will be found that the column measures 60 inches, and so in like proportion as far as the experiment is carried.

The above instrument is better adapted for illustration of the principle than for furnishing rigorous proof of the law. This has, however, been done. MM. Arago and Dulong published, in the year 1830, an account of certain experiments made by them in Paris, in which the law in question had been verified to the extent of twenty-seven atmospheres. With rarefied air, also, of whatever degree of rarefaction, the law has been found true.

All gases are alike subject to this law, and all vapors of volatile liquids, when remote from their points of liquefaction.* It is a matter of the greatest importance in practical chemistry, since it gives the means of making corrections for pressure, or determining by calculation the change of volume which a gas would suffer by any given change of external pressure.

Let it be required, for example, to solve the following problem: We have 100 cubic inches of gas in a graduated jar, the barometer standing at 29 inches; how many cubic inches will it occupy when the column rises to 30 inches? Now the volume must be inversely as the pressure; consequently, a change of pressure in the proportion of 29 to 30 must be accompanied by a change of volume in the proportion of 30 to 29, the 30 cubic inches of gas contracting to 29 cubic inches under the conditions imagined. Hence the answer—

$$30 : 29 = 100 : 96.67 \text{ cubic inches.}$$

The reverse of the operation will be obvious. The pupil will do well to familiarize himself with the simple calculations of corrections for pressure.

* Near the liquefying point the law no longer holds; the volume diminishes *more rapidly* than the theory indicates, a smaller amount of pressure being then sufficient. (See further, p. 66).

HEAT.

It will be convenient to consider the subject of heat under several sections, and in the following order:—

1. Expansion of bodies, or effects of variations of temperature in altering their dimensions.
2. Conduction, or transmission of heat.
3. Specific heat.
4. Change of state.
5. Sources of heat.
6. Dynamical theory of heat.

Expansion.

If a bar of metal of such magnitude as to fit accurately to a gauge, when cold, be heated considerably, and again applied to the gauge, it will be found to have become enlarged in all its dimensions. When cold, it will once more enter the gauge.

Again, if a quantity of liquid contained in a glass bulb furnished with a narrow neck, be plunged into hot water, or exposed to any other source

Fig. 17.

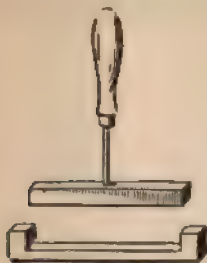


Fig. 18.



Fig. 19.



of heat, the liquid will mount in the stem, showing that its volume has been increased. The bulb, however, has likewise expanded by the heat, and its capacity has consequently been augmented. The rise of the liquid in the tube, therefore, denotes the difference between these two expansions.

Or, if a portion of air be confined in any vessel, the application of a slight degree of heat will suffice to make it occupy a space sensibly larger.

The most general of all the effects of heat furnishes in the outset a principle, by the aid of which an instrument can be constructed capable of taking cognizance of changes of temperature in a manner equally accurate and convenient: such an instrument is the thermometer.

A capillary glass tube is chosen, of uniform diameter; one extremity is

closed and expanded into a bulb, by the aid of the blowpipe flame, and the other somewhat drawn out, and left open. The bulb is now cautiously heated by a spirit-lamp, and the open extremity plunged into a vessel of mercury, a portion of which rises into the bulb when the latter cools, replacing the air which had been expanded and driven out by the heat. By again applying the flame, and causing this mercury to boil, the remainder of the air is easily expelled, and the whole space filled with mercurial vapor. The open end of the tube must now be immediately plunged into the vessel filled with mercury. As the metallic vapors condense, the pressure of the external air forces the liquid metal into the instrument, until finally the tube is completely filled with mercury. The thermometer thus filled is now to be heated until so much mercury has been driven out by the expansion of the remainder, that its level in the tube shall stand at common temperatures at the point required. This being satisfactorily adjusted, the heat is once more applied, until the column rises quite to the top, and then the extremity of the tube is horizontally sealed by the blowpipe. The retraction of the mercury on cooling now leaves an empty space, which is essential to the perfection of the instrument.

The thermometer has yet to be graduated; and to make its indications comparable with those of other instruments, a scale, having at the least two fixed points, must be adapted to it.

It has been observed, that the temperature of melting ice, that is to say, of a mixture of ice and water, is always constant; a thermometer, already graduated, plunged into such a mixture, always marks the same degree of temperature, and a simple tube filled in the manner described and so treated, exhibits the same effect in the unchanged height of the little mercurial column, when tried from day to day. The freezing point of water, or melting point of ice, constitutes then one of the invariable temperatures demanded.

Another is to be found in the boiling point of water, or, more accurately, in the temperature of steam which rises from boiling water. In order to give this temperature, which remains perfectly constant whilst the barometric pressure is constant, to the mercury of the thermometer, distilled water is made to boil in a glass vessel with a long neck, when the pressure is at 30 inches (fig. 20). The thermometer is then so placed that all the mercury is surrounded with steam. It quickly rises to a fixed point, and there it remains as long as the water boils, and the height of the barometer is unchanged.

The tube having been carefully marked with a file at these two points, it remains to divide the interval into degrees; this division is entirely arbitrary. The scale now most generally employed is the Centigrade, in which the space is divided into 100 parts, the zero being placed at the freezing point of water. The scale is continued above and below these points, numbers below 0 being distinguished by the negative sign.

In England and North America the division of Fahrenheit is still in use, the above mentioned space is divided into 180 degrees; but the zero, instead of starting from the freezing point of water, is placed 32 degrees below it, so that the temperature of ebullition is expressed by 212°.

The plan of Beaumur is nearly confined to a few places in the north of Germany and to Russia; in this scale the freezing point of water is made 0°, and the boiling point 50°.

It is unfortunate that a uniform system has not been generally adopted

Fig. 20



in graduating thermometers; this would render unnecessary the labor which now so frequently has to be performed of translating the language of one scale into that of another. To effect this, presents, however, no great difficulty. Let it be required, for example, to know the degree of Fahrenheit's scale which corresponds to 60°C .

$$100^{\circ}\text{C.} = 180^{\circ}\text{F.}; \text{ or } 5^{\circ}\text{C.} = 9^{\circ}\text{F.}$$

Consequently,

$$5 : 9 = 60 : 108.$$

But then, as Fahrenheit's scale commences with 32° instead of 0° , that number must be added to the result, making $60^{\circ}\text{C.} = 140^{\circ}\text{F}$.

The rule, then, is the following: To convert centigrade degrees into Fahrenheit degrees, multiply by 9, divide the product by 5, and add 32; to convert Fahrenheit degrees into centigrade degrees, subtract 32, multiply by 5, and divide by 9.

The reduction of negative degrees, or those below zero, of one scale into those of another scale, is effected in the same way. For example, to convert -15°C . into degrees of Fahrenheit, we have—

$$-15 \times \frac{9}{5} + 32 = -27 + 32 = +5\text{ F.}$$

In this work temperatures will always be given in centigrade degrees, unless the contrary is stated.

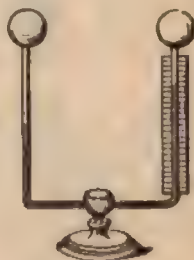
Mercury is usually chosen for making thermometers, on account of its regularity of expansion within certain limits, and because it is easy to have the scale of great extent, from the large interval between the freezing and boiling points of the metal. Other substances are sometimes used; alcohol is employed for estimating very low temperatures, because this liquid has not been frozen even at the lowest degree of cold which has been artificially produced.

Air-thermometers are also used for some few particular purposes; indeed, the first thermometer ever made was of this kind. There are two modifi-

Fig. 21.



Fig. 22.



cations of this instrument; in the first, the liquid into which the tube dips is open to the air; and in the second, shown in Fig. 22, the atmosphere is completely excluded. The effects of expansion are in the one case complicated with those arising from changes of pressure, and in the

other they cease to be visible at all when the *whole* instrument is subjected to alterations of temperature, because the air in the upper and lower reservoir, being equally affected by such changes, no alteration in the height of the fluid column can occur. Accordingly, such instruments are called *differential* thermometers, since they serve to measure differences of temperature between the two portions of air, while changes affecting both alike are not indicated. Fig. 22 shows another form of the same instrument.

The air-thermometer may be employed for measuring all temperatures from the lowest to the highest; M. Pouillet has described one by which the heat of an air-furnace could be measured. The reservoir of this instrument is of platinum, and it is connected with a piece of apparatus by which the increase of volume experienced by the included air is determined.

An excellent air-thermometer has been constructed and used by Rudberg, and more recently by Magnus and Regnault, for measuring the expansion of the air. Its construction depends on the law, that when air is heated and hindered from expanding, its tension increases in the same proportion in which it would have increased in volume if permitted to expand.

All bodies are enlarged by the application of heat, and reduced by its abstraction: or, in other words, contract on being artificially cooled; this effect takes place to a comparatively small extent with solids, to a larger amount in liquids, and most of all in the case of gases.

Each solid and liquid has a rate of expansion peculiar to itself; gases, on the contrary, expand nearly alike for the same increase of heat.

Expansion of Solids.—The actual amount of expansion which different solids undergo by the same increase of heat has been carefully investigated. The following are some of the results of the best investigations, more particularly those of Lavoisier and Laplace. The fraction indicates the amount of expansion in length suffered by the rods of the under-mentioned bodies in passing from 0° to 100°:—

| | | | |
|-------------------------------|------------------|--------------------------|-----------------|
| For wood* | $\frac{5}{1057}$ | Tempered steel | $\frac{1}{187}$ |
| English flint glass | $\frac{1}{1211}$ | Soft iron | $\frac{5}{516}$ |
| Platinum | $\frac{1}{1137}$ | Gold | $\frac{2}{217}$ |
| Common white glass | $\frac{1}{1150}$ | Copper | $\frac{5}{513}$ |
| Common white glass | $\frac{1}{1147}$ | Brass | $\frac{3}{315}$ |
| Glass without lead | $\frac{1}{1111}$ | Silver | $\frac{3}{313}$ |
| Another specimen | $\frac{1}{1060}$ | Lead | $\frac{1}{181}$ |
| Steel untempered | $\frac{5}{517}$ | Zinc | $\frac{3}{313}$ |

From the *linear* expansion, the *cubic* expansion (or measure of volume), may be calculated. When the expansion of a body in different directions is equal, as, for example, in glass, hammered metals, and generally in most uncrystallized substances, it will be sufficient to triple the fraction expressing the increase in one dimension. This rule does not hold true for crystals belonging to irregular systems, for they expand unequally in the direction of the different axes.

Metals appear to expand pretty uniformly for equal increments of heat within the limits stated; but above the boiling point of water the rate of expansion becomes irregular and more rapid.

The *forces* exerted in the act of expansion is very great. In laying down railways, building iron bridges, erecting long ranges of steam-pipes, and in executing all works of the kind in which metal is largely used, it is indispensable to make provision for these changes of dimensions.

* In the direction of the vessels.

should be inversely as their densities. By the aid of the outer cylinders, one of the tubes is maintained constantly at 0° , while the other is raised, by means of heated water or oil, to any required temperature. The perpendicular height of the columns may then be read off by a horizontal anemometer telescope, moving on a vertical divided scale.

These heights represent volumes of equal weight, because volumes of equal weight bear an inverse proportion to the densities of the liquids, so that the amount of expansion admits of being very easily calculated. Thus, let the column at 0° be 6 inches high, and that at 100° , 6.108 inches; the increase of height, 108 on 6000, or $\frac{1}{55.5}$ part of the whole, will represent the absolute cubical expansion.

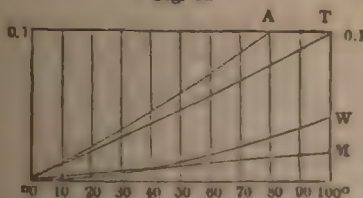
Fig. 23.



The indications of the mercurial thermometer are inaccurate when very high ranges of temperature are concerned, from the increased expansibility of the metal. The error thus caused is, however, nearly compensated, for temperatures under 204.5° C. (400° F.) by the expansion of the glass tube. For higher temperatures a small correction is necessary, as the above table shows.

To what extent the expansion of different liquids may vary between the same temperatures is obvious from a glance at fig. 24 which represents the

Fig. 24.



expansion of mercury (M), water (W), oil of turpentine (T), and alcohol (A). A column of these several liquids, equalling at 0° the tenfold height of the line 0-0.1 in the diagram, would exhibit, when heated to a temperature of 10° , 20° , 30° , etc., an expansion indicated by the distances at which the perpendicular lines drawn over the numbers 10, 20, 30, etc., are intersected by the curves belonging to each of these liquids. Thus it is seen that oil of turpentine, between 0° and 100° , expands very nearly $\frac{1}{10}$ of its volume, and that mercury between the same limits of temperature expands *undecimally*, while the rate of expansion of the other liquids increases with the rise of the temperature.

An exception to the regularity of expansion in liquids exists in the case of water; it is so remarkable, and its consequences so important, that it is necessary to advert to it particularly.

Let a large thermometer-tube be filled with water at the common temperature of the air, and then artificially cooled. The liquid will be observed to contract, until the temperature falls to about 4°C . (39.2°F ., or 7.2° above the freezing point). After this a further reduction of temperature causes expansion instead of contraction in the volume of the water, and this expansion continues until the liquid arrives at its point of congelation, when so sudden and violent an enlargement takes place that the vessel is almost invariably broken. At the temperature of 4° water is at its maximum density; increase or diminution of heat produces upon it, for a short time, the same effect.

According to the latest researches of Kopp, the point of greatest density of water is 4.08°C . (39.34°F .). According to the determinations of this physicist, the volume of water = 1 at 0°C . changes, when heated, to the following volumes:—

| | | | |
|----------------------|----------------------|----------------------|-----------------------|
| 2° 0.99991 | 16° 1.00085 | 35° 1.00570 | 70° 1.02225 |
| 4° 0.99988 | 18° 1.00118 | 40° 1.00753 | 75° 1.02544 |
| 6° 0.99990 | 20° 1.00157 | 45° 1.00954 | 80° 1.02858 |
| 8° 0.99999 | 22° 1.00200 | 50° 1.01177 | 85° 1.03189 |
| 10° 1.00012 | 24° 1.00247 | 55° 1.01410 | 90° 1.03540 |
| 12° 1.00031 | 25° 1.00272 | 60° 1.01659 | 95° 1.03909 |
| 14° 1.00056 | 30° 1.00406 | 65° 1.01930 | 100° 1.04299 |

Sea-water has no point of maximum density above the freezing point. The more it is cooled the denser it becomes, until it solidifies at -2.6°C .

The gradual expansion of pure water cooled below 4°C . must be carefully distinguished from the great and sudden increase of volume it exhibits in the act of freezing, in which respect it resembles many other bodies which expand on solidifying. The force thus exerted by freezing water is enormous. Thick iron shells quite filled with water, and exposed with their fuse-holes securely plugged, to the cold of a Canadian winter night, have been found split on the following morning. The freezing of water in the joints and crevices of rocks is a most potent agent in their disintegration.

Expansion of Gases.—The principal laws relating to the expansion of gases are contained in the four following propositions:—

1. All gases expand nearly alike for equal increments of heat; and all vapors, when remote from their condensing points, follow the same law.
2. The rate of expansion is not altered by a change in the state of compression, or elastic force, of the gas itself.
3. The rate of expansion is uniform for all degrees of heat.
4. The actual amount of expansion is equal to $\frac{1}{273}$ or $\frac{1}{273.15}$ or 0.003660 of the volume of the gas at 0° centigrade, for each degree of the same scale.*

It will not be necessary to enter into any description of the methods of investigation by which these results have been obtained; the advanced student will find in Pouillet's "*Éléments de Physique*," and in the papers of Magnus and Regnault,† all the information he may require.

* The fraction $\frac{1}{273}$ is very convenient for calculation.

† Poggendorff's *Annalen*, iv. 1—*Ann. Chim. Phys.* 3d series, iv. 5, and v. 53. See also Watts's *Dictionary of Chemistry*, art. Heat, vol. iii. p. 46; and Ganot's *Éléments de Physique*, translated by Dr. Atkinson, 4th edition, pp. 238-262.

In the practical manipulation of gases, it very often becomes necessary to make a correction for temperature, or to discover how much the volume of a gas would be increased or diminished by a particular change of temperature; this can be effected with great facility. Let it be required, for example, to find the volume which 100 cubic inches of any gas at 10° C. would become on the temperature rising to 20° C.

The rate of expansion is $\frac{1}{273}$ of the volume at 0° for each degree; or 3000 measures at 0° become 3011 at 1° , 3022 at 2° , 3110 at 10° , and 3220 at 20° . Hence

$$\begin{array}{ccccccc} \text{Meas. at } 10^{\circ}. & & \text{Meas. at } 20^{\circ}. & & \text{Meas. at } 10^{\circ}. & & \text{Meas. at } 20^{\circ}. \\ 3110 & : & 3220 & = & 100 & : & 103.537. \end{array}$$

If this calculation is required to be made on the Fahrenheit scale, it must be remembered that the zero of that scale is 32° below the melting-point of ice. Above this temperature the expansion for each degree of the Fahrenheit scale is $\frac{1}{273}$ of the original volume.

This, and the correction for pressure, are operations of very frequent occurrence in chemical investigations, and the student will do well to become familiar with them.

The following formula includes both these corrections: Let V and V' be the volume of a gas at the temperatures t and t' centigrade, and under the pressure p and p' , measured in millimetres of mercury: then

$$\frac{V}{V'} = \frac{1 + 0.00366t}{1 + 0.00366t'} \cdot \frac{p'}{p}$$

The case which most frequently occurs is the reduction of a measured volume, V , of a gas at the temperature t and pressure p to the volume V_0 , which it would occupy at 0° C., and under a pressure of 760 mm. In this case, we have $t' = 0$, and $p' = 760$, therefore

$$\frac{V}{V_0} = (1 + 0.00366t) \cdot \frac{760}{p},$$

and

$$V_0 = \frac{V}{1 + 0.00366t} \cdot \frac{p}{760}.$$

If the barometric pressure is measured in inches, the number 30 must be substituted for 760.

Note.—If the four propositions stated in the text, the first and second have essentially been shown to be true within certain limits only; and the third, although in the highest degree probable, would be very difficult to demonstrate rigidly; in fact, the equal rate of expansion of air is assumed in all experiments on other substances, and becomes the standard by which the results are measured.

The rate of expansion for the different gases is *not* absolutely the same, but the difference is so small that for most purposes it may safely be neglected. Neither is the state of elasticity altogether indifferent, the expansion being sensibly greater for an equal rise of temperature when the gas is in a compressed state.

It is important to notice that the greatest deviations from the rule are exhibited by those gases which, as will hereafter be seen, are most easily liquefied, such as carbon dioxide, cyanogen, and sulphur dioxide; and that the discrepancies become smaller and smaller as the elastic force is lessened, so that, if means existed for comparing the different gases in states

equally distant from their points of condensation, there is reason to believe that the law would be strictly fulfilled.

The experiments of Dalton and Gay-Lussac gave for the rate of expansion $\frac{1}{273}$ of the volume at 0° : this is no doubt too high. Those of Rudberg give $\frac{1}{274}$, those of Magnus and of Regnault $\frac{1}{273}$.

Conduction of Heat.

Different bodies possess very different conducting powers with respect to heat: if two similar rods, the one of iron, the other of glass, be held in the flame of a spirit-lamp, the iron will soon become too hot to be touched, while the glass may be grasped with impunity within an inch of the red-hot portion.

Experiments made by analogous but more accurate methods have established a numerical comparison of the conducting powers of many bodies. The following may be taken as a specimen:—

| | | | |
|------------------|------|-------------------------|-----|
| Silver | 1000 | Steel | 116 |
| Copper | 736 | Lead | 85 |
| Gold | 532 | Platinum | 84 |
| Brass | 236 | German silver | 63 |
| Tin | 145 | Bismuth | 18 |
| Iron | 119 | | |

As a class the metals are by very far the best conductors, although much difference exists between them; stones, dense woods, and charcoal follow next in order; then liquids in general, and lastly gases, whose conducting power is almost inappreciable.

Under favorable circumstances, nevertheless, both liquids and gases may become rapidly heated: heat applied to the bottom of the containing vessel is very speedily communicated to its contents; this, however, is not so much by conduction, as by convection, or carrying. A complete circulation is set up: the portions in contact with the bottom of the vessel get heated, become lighter, and rise to the surface, and in this way the heat becomes communicated to the whole. If these movements be prevented by dividing the vessel into a great number of compartments, the really low conducting power of the substance is made evident; and this is the reason why certain organic fabrics, as wool, silk, feathers, and porous bodies in general, the cavities of which are full of air, exhibit such feeble powers of conduction.

The circulation of heated water through pipes is now extensively applied to the warming of buildings and conservatories; and in chemical works a serpentine metal tube containing hot oil is often used for heating stills and evaporating pans; the two extremities of the tube are connected with the ends of another spiral built into a small furnace at a lower level, and an unintermitting circulation of the liquid takes place as long as heat is applied.

Specific Heat.

Equal weights of different substances having the same temperature require different amounts of heat to raise them to a given degree of temperature. If 1 lb. of water, at 100° , be mixed with 1 lb. at 40° , then, as is well known, a mean temperature of $\frac{100 + 40}{2} = 70^\circ$ is obtained. In the

same way the mean temperature is found when warm and cold oil, or warm and cold mercury, etc., are mixed together. But if 1 lb. of water at 100° be shaken with 1 lb. of olive-oil at 40° , or with 1 lb. of mercury at 40° , then, instead of the mean temperature of 70° , the temperature actually

desired will be 80° in the first case, 98° in the second; 20 degrees of heat which the water (by cooling from 100° to 80°) gave to the same weight of oil, were sufficient to raise the oil 40° , that is, from 40° to 80° ; and 2°, which the water lost by cooling from 100° to 98° , sufficed to heat an equal quantity of mercury 58° , namely from 40° to 98° .

It is evident from these experiments that the quantities of heat which equal weights of water, olive-oil, and mercury, require to raise their temperature to the same height, are unequal, and that they are in the proportion of the numbers $1 : \frac{3}{4} : \frac{1}{2}$, or $1 : \frac{1}{2} : \frac{1}{4}$.

These quantities of heat, expressed relatively to the quantity of heat required to raise the temperature of an equal weight of water from 0° to 1° , are called the specific heats of the various substances; thus the experiments just described show that the specific heat of olive-oil is $\frac{1}{2}$, that is to say, the quantity of heat which would raise the temperature of any given quantity of olive-oil from 0° to 1° would raise that of an equal weight of water only from 0° to $\frac{1}{2}^{\circ}$, or of half that quantity of water from 0° to 1° .

The specific heats of bodies are sometimes said to measure their relative capacities for heat.

There are three distinct methods by which the specific heats of various substances may be estimated. The first of these is by observing the quantity of ice melted by a given weight of the substance heated to a particular temperature; the second is by noting the time which the heated body requires to cool down through a certain number of degrees; and the third is the method of mixture, on the principle illustrated; this latter method is preferred as the most accurate.

The determination of the specific heat of different substances has occupied the attention of many experimenters; among these Dulong and Petit, and recently Regnault and Kopp, deserve especial mention.

From the observations of these and other physicists, it follows that each body has its peculiar specific heat, and that the specific heat increases with increase of temperature. If, for example, the heat which the unit of water loses by cooling from 10° to 0° be marked at 10° , then the loss by cooling from 50° to 0° will be, not 50, corresponding to the difference of temperature, but 50.1. By cooling from 100° to 0° it is 100.5, and rises to 203.2 when the water is heated under great pressure to 200° , and afterwards cooled to 0° . Similar and even more striking differences have been found with other substances. It has also been proved that the specific heat of any substance is greater in the liquid than in the solid state. For example, the specific heat of ice is 0.504, that is, not more than half as great as that of liquid water.

It is remarkable that the specific heat of water is greater than that of all other solid and liquid substances, and is exceeded only by that of hydrogen. The specific heat of the solid parts of the crust of the globe is on an average $\frac{1}{4}$, and that of the atmosphere nearly $\frac{1}{2}$ that of water.

If the specific heat of any body within certain degrees of temperature be accurately known, then from the quantity of heat which this body gives out when quickly dipped into cold water, the temperature to which the body was heated may be determined. Pouillet has founded on this fact a method of measuring high temperatures, and for this purpose, with the help of the air-thermometer, he has determined the specific heat of platinum up to 1600° C.

The determination of the specific heat of gases is attended with peculiar difficulties, on account of the comparatively large volume of small weights of gases. For many gases, however, satisfactory results have been obtained by the method of mixing.

When a gas expands, heat becomes latent, that is to say, insensible to

the thermometer; in fact, the molecular motion which constitutes heat is converted into another kind of motion, which overcomes the pressure to which the gas is subjected, and allows it to expand (see page 78). The amount of heat required, therefore, to raise a gas to any given temperature increases the more the gas in question is allowed to expand. The quantity of heat which the unit-weight of a gas requires in order to raise its temperature 1° without its volume undergoing any change (which can take place only by the pressure being simultaneously augmented) is called the specific heat of the gas *at constant volume*. The quantity of heat required by the unit-weight of a gas to raise its temperature 1° , it being at the same time allowed to dilate to such an extent that the pressure to which it is exposed remains unchanged, is called the specific heat of the gas *at constant pressure*. According to what has already been stated, the specific heat at constant pressure must be greater than that at constant volume. Dulong found, in the case of atmospheric air, of oxygen, of hydrogen, and of nitrogen, that the two specific heats are in the proportion 1.421 : 1. For carbon monoxide, however, he obtained the proportion of 1.423, for carbon dioxide 1.337, for nitrogen dioxide 1.343, and for olefiant gas 1.24 to 1. The exact determination of these ratios is extremely difficult, and the results of different physicists by no means agree.

The first satisfactory comparison of the specific heat of air with that of water was made by Count Rumford; later comparisons of the specific heat of various gases have been made by Delaroche and Bérard, Dulong and Regnault.

The first researches of Delaroche and Bérard furnished the results embodied in the following table:—

| | Equal volumes | | Equal weights. | |
|-----------------------------|-----------------------|------------------------|-----------------|--------|
| | The volumes constant. | The pressure constant. | Air=1. Water=1. | |
| Atmospheric air | 1 | 1 | 1 | 0.2669 |
| Oxygen | 1 | 1 | 0.9045 | 0.2414 |
| Hydrogen | 1 | 1 | 14.4510 | 3.8569 |
| Nitrogen | 1 | 1 | 1.0295 | 0.2748 |
| Carbon monoxide | 1 | 1 | 1.0337 | 0.2759 |
| Nitrogen monoxide | 1.227 | 1.160 | 0.7607 | 0.2030 |
| Carbon dioxide | 1.249 | 1.175 | 0.7685 | 0.2051 |
| Olefiant gas | 1.754 | 1.531 | 1.5829 | 0.4225 |

The latest and most trustworthy determinations are those of Regnault, given in the subjoined table, in the second column of which the specific heats of the several gases and vapors are compared with that of an equal weight of water taken as unity, and in the third, with that of an equal volume of air referred to its own weight of water as unity. The latter series of numbers is obtained by multiplying the numbers in the second column by the specific gravities of the respective gases and vapors referred to air as unity:—

| Gases. | Specific gravity.
Air=1. | Specific heat
at constant pressure. | |
|---------------------------|-----------------------------|--|--------------------|
| | | For equal weights.
Water = 1. | For equal volumes. |
| Atmospheric air | 1 | 0.2377 | 0.2377 |
| Oxygen | 1.1056 | 0.2175 | 0.2405 |
| Nitrogen | 0.9713 | 0.2438 | 0.2368 |
| Hydrogen | 0.0692 | 3.4090 | 0.2359 |
| Chlorine | 2.4502 | 0.1210 | 0.2965 |
| Bromine vapor | 5.4772 | 0.0555 | 0.3040 |

| Gases. | Specific gravity.
Air = 1. | Specific heat
at constant pressure. | |
|--------------------------------------|-------------------------------|--|--------------------|
| | | For equal weights.
Water = 1. | For equal volumes. |
| Carbon monoxide | 0.9670 | 0.2450 | 0.2370 |
| Carbon dioxide | 1.5210 | 0.2169 | 0.3307 |
| Nitrogen monoxide | 1.5241 | 0.2262 | 0.3447 |
| Nitrogen dioxide | 1.0384 | 0.2317 | 0.2406 |
| Olefiant gas | 0.9672 | 0.4040 | 0.4106 |
| Marsh gas | 0.5527 | 0.5929 | 0.3277 |
| Aqueous vapor | 0.6220 | 0.4805 | 0.2989 |
| Sulphuretted hydrogen | 1.1746 | 0.2432 | 0.2857 |
| Sulphur dioxide | 2.2112 | 0.1544 | 0.3414 |
| Vapor of carbon bisulphide | 2.6258 | 0.1509 | 0.4122 |
| Hydrochloric acid | 1.2596 | 0.1862 | 0.2333 |
| Ammonia | 0.5894 | 0.5084 | 0.2996 |

The researches of Delaroche and Bérard led them to suppose that the specific heat of gases increased rapidly as the temperature was raised, and that for a given volume of gas it increased in proportion to the density or tension of the gas. Regnault found, however, the quantity of heat which a given volume of gas requires to raise it to a certain temperature, to be independent of its density; and that for each degree between -30°C . and 225°C . it is constant. Carbon dioxide, however, forms an exception to this rule, its specific heat increasing with the temperature. In the table mean values for temperatures between 10°C . and 200°C . have been given.

Several physicians have held that the specific heats of elementary gases, referred to equal volumes, are identical. The numbers which Regnault found for chlorine and bromine, however, show that the law does not hold good for all elementary gases.

It has been already stated that, when a gas expands, heat becomes latent. If a gas on expanding be not supplied with the requisite heat, its temperature falls on account of its own free heat becoming latent, that is, expended in overcoming pressure. On the other hand, if a gas be compressed, this latent heat becomes free, and causes an elevation of temperature, which, under favorable circumstances, may be raised to ignition; syringes by which tinder is kindled are constructed on this principle.

Change of State.

1. Fusion and Solidification.

Solid bodies when heated are expanded; many are liquefied, *i. e.*, they melt or fuse. The melting of solids is frequently preceded by a gradual softening, more especially when the temperature approaches the point of fusion. This phenomenon is observed in the case of wax or iron. In the case of other solids—of zinc and lead, for instance—and several other metals, this softening is not observed. Generally, bodies expand during the process of fusion; an exception to this rule is water, which expands during freezing (10 vol. of water produce nearly 11 vol. of ice), while ice when melting produces a proportionately smaller volume of water. The expansion of bodies during fusion, and at temperatures preceding fusion, or the contraction during solidification and further refrigeration, is very unequal. Wax expands considerably before fusing, and comparatively little during fusing itself. Wax, when poured into moulds, fills them perfectly during solidification, but afterwards contracts considerably.

Stearic acid, on the contrary, expands very little before fusion, but rather considerably during fusion, and consequently pure stearic acid when poured into moulds solidifies to a rough porous mass contracting little by further cooling. The addition of a little wax to stearic acid prevents the powerful contraction in the moment of solidification, and renders it more fit for being moulded.

Latent Heat of Fusion.—During fusion bodies absorb a certain quantity of heat, which is not indicated by the thermometer; at a given temperature—the melting point, for instance—a certain weight of substance contains when solid less heat than when liquid.

If equal weights of water at 0° C. (32° F.) and water at 79° C. (174.2° F.) be mixed, the temperature of the mixture will be the mean of the two temperatures, or 39.5° . If the same experiment be repeated with snow or finely-powdered ice at 0° , and water at 79° , the temperature of the whole will be only 0° , but the ice will have been melted.

$$\begin{array}{lcl} 1 \text{ lb. of water at } 0^{\circ} & \} & \\ 1 \text{ lb. of water at } 79^{\circ} & \} & = 2 \text{ lb. water at } 39.5^{\circ}. \\ 1 \text{ lb. of ice at } 0^{\circ} & \} & \\ 1 \text{ lb. of water at } 79^{\circ} & \} & = 2 \text{ lb. water at } 0^{\circ}. \end{array}$$

In the last experiment, therefore, as much heat has been apparently lost as would have raised a quantity of water equal to that of the ice through a range of 79° (142.2° F.).

The heat, thus become insensible to the thermometer in effecting the liquefaction of the ice, is called latent heat, or better, heat of fluidity.

Again, let a perfectly uniform source of heat be imagined, of such intensity that a lb. of water placed over it would have its temperature raised 5° per minute. Starting with water at 0° , in rather less than 16 minutes its temperature would have risen 79° ; but the same quantity of ice at 0° , exposed for the same interval of time, would not have its temperature raised a single degree. But, then, it would have become water; the heat received would have been exclusively employed in effecting the change of state.

This heat is not lost, for when the water freezes it is again evolved. If a tall jar of water, covered to exclude dust, be placed in a situation where it shall be quite undisturbed, and at the same time exposed to great cold, the temperature of the water may be reduced 10° C. (18° F.) or more below its freezing point without the formation of ice;* but then, if a little agitation be communicated to the jar, or a grain of sand dropped into the water, a portion instantly solidifies, and the temperature of the whole rises to 0° ; the heat disengaged by the freezing of a small portion of the water is sufficient to raise the whole contents of the jar 5° C. (9° F.).

This curious condition of instable equilibrium shown by the very cold water in the preceding experiment, may be reproduced with a variety of solutions which tend to crystallize or solidify, but in which that change is for a while suspended. Thus, a solution of crystallized sodium sulphate in its own weight of warm water, left to cool in an open vessel, deposits a large quantity of the salt in crystals. If the warm solution, however, be

* Fused bodies, when cooled down to or below their fusing point, frequently remain liquid, more especially when not in contact with solid bodies. Thus, water in a mixture of oil of almonds and chloroform, of specific gravity equal to its own, remains liquid to -10° ; in a similar manner fused sulphur or phosphorus, floating in a solution of zinc chloride of appropriate concentration, retains the liquid condition at temperatures 40° below its fusing point. Liquid bodies, thus cooled below their fusing point, frequently solidify when touched with a solid substance, invariably when brought in contact with a fragment of the same body in the solid state. A body thus retained in the liquid state below its ordinary solidifying point, is said to be in a state of *superfusion* or *superfusion*.

filtered into a clean flask, which when full is securely corked and set aside undisturbed, no crystals will be deposited, even after many days, until the cork is withdrawn and the contents of the flask are violently shaken. Crystallization then rapidly takes place in a very beautiful manner, and the whole becomes perceptibly warm. The law above illustrated in the case of water is perfectly general. Whenever a solid becomes a liquid, a certain fixed and definite amount of heat disappears, or becomes latent; and conversely, whenever a liquid becomes solid, heat to a corresponding extent is given out.

The following table exhibits the melting points of several substances, and their latent heats of fusion expressed in gram-degrees—that is to say, the numbers in the column headed “latent heat” denote the number of grams of water, the temperature of which would be raised 1° centigrade by the quantity of heat required to fuse one gram of the several solids:—

| Substance. | Melting Point. | Latent Heat. | Substance. | Melting Point. | Latent Heat. |
|----------------------|----------------|--------------|---|----------------|--------------|
| Mercury | -39° | 2.82 | Tin | 235° | 14.25 |
| Phosphorus | $+44$ | 5.0 | Silver | 1000 | 21.1 |
| Lead | 332 | 5.4 | Zinc | 433 | 28.1 |
| Sulphur | 115 | 9.4 | Calcium chloride }
($\text{CaCl}_2, 6\text{H}_2\text{O}$), } | 28.5 | 40.7 |
| Iodine | 107 | 11.7 | Potassium nitrate . | 339 | 47.4 |
| Bismuth | 270 | 12.6 | Sodium nitrate . . | 310.5 | 63.0 |
| Cadmium | 320 | 13.6 | | | |

Freezing Mixtures.—When a solid substance can be made to liquefy by a weak chemical attraction, cold results, from sensible heat becoming latent. This is the principle of frigorific mixtures. When snow or powdered ice is mixed with common salt, and a thermometer plunged into the mass, the mercury sinks to -17.7° C. (0° F.), while the whole after a short time becomes fluid by the attraction between the water and the salt; such a mixture is very often used in chemical experiments to cool receivers and condense the vapors of volatile liquids. Powdered crystallized calcium chloride and snow produce cold enough to freeze mercury. Even powdered potassium nitrate, or sal-ammoniac, or ammonium nitrate, dissolved in water, occasions a very notable depression of temperature; in every case, a short, in which solution is unaccompanied by energetic chemical action, cold is produced.

No relation can be traced between the actual melting point of a substance and its latent heat when in the fused state.

2. Vaporization and Condensation.

A law of exactly the same kind as that above described affects universally the gaseous condition; change of state from solid or liquid to gas is accompanied by absorption of sensible heat, and the reverse by its disengagement. The latent heat of steam and other vapors may be ascertained by a mode of investigation similar to that employed in the case of water.

When water at 0° C. is mixed with an equal weight of water at 100° C., the mixture is found to possess the mean of the two temperatures, or 50° ; on the other hand, 1 part by weight of steam at 100° C., when condensed in cold water, is found to be capable of raising 5.4 parts of the latter from the freezing to the boiling point, or through a range of 100° C. Now $100 \times 5.4 = 540^{\circ}$; that is to say, steam at 100° C. in becoming water at 100° C., parts with enough heat to raise a weight of water equal to its own (if it

were possible) 540° of the thermometer, or 540 times its own weight of water one degree. When water passes into steam the same quantity of sensible heat becomes latent.

The vapors of other liquids seem to have less latent heat than that of water. The following table is by Dr. Andrews, of Belfast, and serves well to illustrate this point. The latent heats are expressed, as in the last table, in gram-degrees :—

| | | Latent Heat. |
|---------------------|-----------|---------------------|
| Vapor of water | | 535.90 ^o |
| " alcohol | | 202.40 |
| " ether | | 90.45 |
| " oxalic ether | | 72.72 |
| " acetic ether | | 92.68 |
| " ethylic iodide | | 46.87 |
| " wood spirit | | 263.70 |
| " carbon bisulphide | | 86.67 |
| " tin tetrachloride | | 30.35 |
| " bromine | | 45.66 |
| " oil of turpentine | | 74.03 |

Boiling or Ebullition is occasioned by the formation of bubbles of vapor within the body of the evaporating liquid, which rise to the surface like bubbles of permanent gas. This occurs in different liquids at very different temperatures. Under the same circumstances, the boiling point is quite constant, and often becomes a physical character of great importance in distinguishing liquids which much resemble each other. A few cases may be cited in illustration :—

| Substance. | Boiling Point. | |
|-------------------------------|----------------------|-------------------------|
| Aldehyde | 20.8 ^o C. | (69.4 ^o F.) |
| Ether | 34.9 | (94.8) |
| Carbon bisulphide | 46.1 | (116.4) |
| Alcohol | 78.4 | (173.1) |
| Water | 100 | (212) |
| Nitric acid, strong | 120 | (248) |
| Oil of turpentine | 157 | (314.6) |
| Sulphuric acid | 326.6 | (439.2) |
| Mercury | 350 | (662) |

For ebullition to take place, it is necessary that the elasticity of the vapor should be able to overcome the cohesion of the liquid and the pressure upon its surface; hence the extent to which the boiling point may be modified.

Water, under the usual pressure of the atmosphere, boils at 100° (212° F.); in a partially exhausted receiver, or on a mountain-top, it boils at a

Fig. 25.



much lower temperature; and in the best vacuum of an air-pump, over oil of vitriol, which absorbs the vapor, it will often enter into violent ebullition while ice is in the act of forming upon the surface.

On the other hand, water confined in a very strong metallic vessel may be restrained from boiling by the pressure of its own vapor to an almost unlimited extent; a temperature of 177° or 204° is very easily obtained, and, in fact, it is said that water may be made red-hot, and yet retain its liquidity.

There is a very simple and beautiful experiment illustrative of the effect of diminished pressure in lowering the

boiling point of a liquid. A little water is made to boil for a few minutes in a flask or retort placed over a lamp, until the air has been chased out, and the steam issues freely from the neck. A tightly-fitting cork is then inserted, and the lamp at the same moment withdrawn. When the boiling ceases, it may be renewed at pleasure for a considerable time by pouring cold water on the flask, so as to condense the vapor within, and occasion a partial vacuum.

The nature of the vessel, or, rather, the state of its surface, exercises an influence upon the boiling point, and this to a much greater extent than was formerly supposed. It has long been noticed that in a metallic vessel water boils, under the same circumstances of pressure, at a temperature one or two degrees below that at which ebullition takes place in glass; but by particular management a much greater difference can be observed. If two similar glass flasks be taken, the one coated in the inside with a film of shellac, and the other completely cleansed by hot sulphuric acid, water heated over a lamp in the first will boil at 99.4°C , while in the second it will often rise to 105° or even higher; a momentary burst of vapor then ensues, and the thermometer sinks a few degrees, after which it rises again. In this state, the introduction of a few metallic filings, or angular fragments of any kind, occasions a lively disengagement of vapor, while the temperature sinks to 100° , and there remains stationary. These remarkable effects must be attributed to an attraction between the surface of the vessel and the liquid.

When out of contact with solid bodies, liquids not only solidify with reluctance, but also assume the gaseous condition with greater difficulty. Drops of water or of aqueous saline solutions floating on the contact-surface of two liquids, of which one is heavier and the other lighter, may be heated from 10 to 20 degrees above the ordinary boiling point; explosive ebullition, however, is instantaneously induced by contact with a solid substance.

A cubic inch of water in becoming steam under the ordinary pressure of the atmosphere expands into 1696 cubic inches, or nearly a cubic foot.

Steam, *not in contact with water*, is affected by heat in the same manner as the permanent gases; its rate of expansion and increase of elastic force are practically the same. When water is present, the rise of temperature increases the quantity and density of the steam, and hence the elastic force increases in a far more rapid proportion.

This elastic force of steam in contact with water, at different temperatures, has been very carefully determined by Arago and Dulong, and lately by Magnus and Regnault. The force is expressed in atmospheres; the absolute pressure upon any given surface can be easily calculated, knowing 14.7 lb. per square inch to each atmosphere. The experiments were carried to twenty-five atmospheres—at which point the difficulties and danger became so great as to put a stop to the inquiry; the rest of the table is the result of calculations founded on the data so obtained:—

| Pressure of Steam
in Atmospheres. | Corresponding
Temperature. | Pressure of Steam
in Atmospheres. | Corresponding
Temperature. |
|--------------------------------------|---|--------------------------------------|---|
| 1 | 100°C . 212°F . | 5.5 | 157°C . 314.6°F . |
| 1.5 | 112 233.6 | 6 | 160 320 |
| 2 | 122 251.6 | 6.5 | 163 325.4 |
| 2.5 | 129 264.2 | 7 | 167 332.4 |
| 3 | 135 275 | 7.5 | 169 336.2 |
| 3.5 | 140.5 284 | 8 | 172 341.6 |
| 4 | 145.5 293.9 | 9 | 177 350.6 |
| 4.5 | 149 300.2 | 10 | 182 359.6 |
| 5 | 153 307.4 | 11 | 186 365.6 |

| Pressure of Steam
in Atmospheres. | Corresponding
Temperature. | | Pressure of Steam
in Atmospheres. | Corresponding
Temperature. | |
|--------------------------------------|-------------------------------|---------|--------------------------------------|-------------------------------|-----------|
| 12 | 190° C. | 374° F. | 22 | 219° C. | 426.2° F. |
| 13 | 194 | 381.2 | 23 | 222 | 431.6 |
| 14 | 197 | 386.6 | 24 | 224 | 435.2 |
| 15 | 200.5 | 392.9 | 25 | 226 | 438.8 |
| 16 | 203 | 397.4 | 30 | 236 | 456.5 |
| 17 | 207 | 404.6 | 35 | 245 | 473 |
| 18 | 209 | 408.2 | 40 | 253 | 487.4 |
| 19 | 212 | 413.6 | 45 | 255 | 491 |
| 20 | 214 | 417.2 | 50 | 266 | 510.8 |
| 21 | 217 | 422.6 | | | |

It is very interesting to know the amount of heat requisite to convert water of any given temperature into steam of the same or another given temperature. The most exact experiments on this subject have been made by Regnault. He arrived at this result, that when the unit-weight of steam at the temperature t° is converted into water of the same temperature, and then cooled to 0° , it gives out the quantity of heat T , which is represented by the formula:—

$$T = 606.5 + 0.305 t.$$

This formula appears to hold good for temperatures both above and below the ordinary boiling point of water. The following table gives the values of T , corresponding to the respective temperatures in the first column:—

| t | T |
|-----|--------|
| 0° | 606.5° |
| 50 | 621.7 |
| 100 | 637.0 |
| 150 | 652.2 |
| 200 | 667.5 |

T is called the total heat of steam, being the heat required to raise water from 0° to t , together with that which becomes latent by the transformation of water at t° into steam at t° . Regnault states, as a result of some very delicate experiments, that the heat necessary to raise a unit-weight of water from 0° to t° is not exactly denoted by t ; the discrepancy, however, is so small that it may be disregarded. Employing the approximate value, the latent heat of steam, L , at any temperature will be found by subtracting t from the total heat; or, according to the formula:—

$$L = 606.5 - 0.695 t.$$

This equation shows us the remarkable fact that the latent heat of steam diminishes as the temperature rises. Before Regnault's experiments were made, two laws of great simplicity were generally admitted, one of which, however, contradicted the other. Watt concluded, from experiments of his own, as well as from theoretical speculations, that the total heat of steam would be the same at all temperatures. Were this true, equal weights of steam passed into cold water would always exhibit the same heating power, no matter what the temperature of the steam might be. Exactly the same *absolute* amount of heat, and consequently the same quantity of fuel, would be required to evaporate a given weight of water *in vacuo* at a temperature which the hand can bear, or under great pressure and at a high temperature. Watt's law, though agreeing well with the rough practical results obtained by engineers, is only approximately true; and the same may be said of the deductions which have just been made

from it. The second law, in opposition to Watt's, is that of Southern, stating the latent heat of steam to be the same at all temperatures. Regnault's researches have shown that neither Watt's law (J constant) nor Southern's law (L constant) is correct.

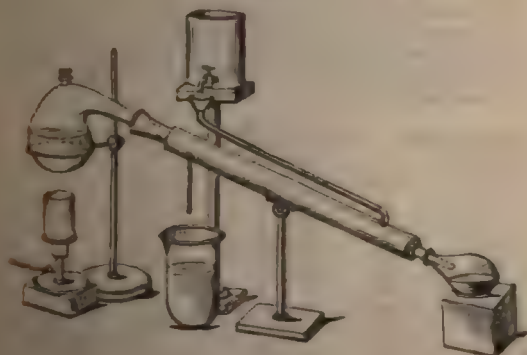
Distillation.—The process of distillation is very simple: its object is either to separate substances which rise in vapor at different temperatures, or to part a volatile liquid from a substance incapable of volatilization. The same process applied to bodies which pass directly from the solid to the

Fig. 26.



gaseous condition, and the reverse, is called *sublimation*. Every distillatory apparatus consists essentially of a boiler, in which the vapor is raised, and of a condenser, in which it returns to the liquid or solid condition. In the small employed for manufacturing purposes, the latter is usually a spiral

Fig. 27.



metal tube immersed in a tub of water. The common retort and receiver constitute the simplest arrangement for distillation on the small scale; the retort is heated by a gas lamp, and the receiver is kept cool, if necessary, by a wet cloth, or it may be surrounded with ice (fig. 26).

Liebig's condenser (fig. 27) is a very valuable instrument in the laboratory; it consists of a glass tube tapering from end to end, fixed by perforated corks in the centre of a metal pipe, provided with tubes so arranged that a current of cold water may circulate through the apparatus. By putting ice into the little cistern, the water may be kept at 0° , and extremely volatile liquids condensed.

Tension of Vapors.—Liquids evaporate at temperatures below their boiling points; in this case the evaporation takes place slowly from the surface. Water, or alcohol, exposed in an open vessel at the temperature of the air, gradually disappears; the more rapidly, the warmer and drier the air.

This fact was formerly explained by supposing that air and gases in general had the power of dissolving and holding in solution certain quantities of liquids, and that this power increased with the temperature; such an idea is incorrect.

If a barometer-tube be carefully filled with mercury and inverted in the usual manner, and then a few drops of water passed up the tube into the vacuum above, a very remarkable effect will be observed—the mercury will be depressed to a small extent, and this depression will increase with increase of temperature. Now, as the space above the mercury is void of air, and the weight of the few drops of water quite inadequate to account for this depression, it must of necessity be imputed to the vapor which instantaneously rises from the water into the vacuum; and that this effect is really due to the elasticity of the aqueous vapor, is easily proved by exposing the barometer to a heat of 100° , when the depression of the mercury will be complete, and it will stand at the same level within and without the tube; indicating that at that temperature the elasticity of the vapor is equal to that of the atmosphere—a fact which the phenomenon of ebullition has already shown.

Fig. 28.



By placing over the barometer a wide open tube dipping into the mercury below (fig. 28), and then filling this tube with water at different temperatures, the tension of the aqueous vapor for each degree of the thermometer may be accurately determined by its depressing effect upon the mercurial column; the same power which forces the latter down one inch against the pressure of the atmosphere, would of course elevate a column of mercury to the same height against a vacuum, and in this way the tension may be conveniently expressed. The following table was drawn up by Dalton, to whom we owe the method of investigation:—

| Temperature. | | Tension in
inches of
mercury. | Temperature. | | Tension in
inches of
mercury. |
|--------------|--------------|-------------------------------------|----------------|---------------|-------------------------------------|
| C. | F. | | C. | F. | |
| 0° | 32° | 0.200 | 54.4° | 130° | 4.34 |
| 4.4 | 40 | 0.263 | 60 | 140 | 5.74 |
| 10 | 50 | 0.375 | 65.5 | 150 | 7.42 |
| 15.5 | 60 | 0.524 | 71.1 | 160 | 9.46 |
| 21.1 | 70 | 0.721 | 76.6 | 170 | 12.13 |
| 26.6 | 80 | 1.000 | 82.2 | 180 | 15.15 |
| 32.2 | 90 | 1.360 | 87.7 | 190 | 19.00 |
| 37.7 | 100 | 1.860 | 93.3 | 200 | 23.64 |
| 43.3 | 110 | 2.530 | 100 | 212 | 30.00 |
| 48.9 | 120 | 3.330 | | | |

Another table representing the tension of the vapor of water, drawn up by Regnault, is given in the Appendix to this work.

Other liquids tried in this manner are found to emit vapors of greater or less tension, for the same temperature, according to their different degrees of volatility; thus a little ether introduced into the tube depresses the mercury 10 inches or more at the ordinary temperature of the air; oil of vitriol, on the other hand, does not emit any sensible quantity of vapor until a much greater heat is applied, and that given off by mercury itself in warm summer weather, although it may be detected by very delicate means, is far too little to exercise any effect upon the barometer. In the case of water, the evaporation is quite distinct and perceptible at the lowest temperatures when frozen to solid ice in the barometer tube; snow on the ground, or on a housetop, may often be noticed to vanish, from the same cause, day by day in the depth of winter, when melting is impossible.

There exists for each vapor a state of density which it cannot pass without losing its gaseous condition, and becoming liquid; this is called the *condition of maximum density*. When a volatile liquid is introduced in sufficient quantity into a vacuum, this condition is always reached, and then evaporation ceases. Any attempt to increase the density of this vapor by compressing it into a smaller space will be attended by the liquefaction of a portion, the density of the remainder being unchanged. If a little ether be introduced into a barometer, and the latter slowly sunk into a very deep cistern of mercury (fig. 29), it will be found that the height of the column of mercury in the tube above that in the cistern remains unaltered until the upper extremity of the barometer approaches the surface of the metal in the column, and all the ether has become liquid. It will be observed also, that, as the tube sinks, the stratum of liquid ether increases in thickness, but no increase of elastic force occurs in the vapor above it, and consequently, no increase of density; for tension and density are always, under ordinary circumstances at least, directly proportionate to each other.

The maximum density of vapors is dependent upon the temperature, it increases rapidly as the temperature rises. This is well shown in the case of water. Thus, taking the spec. grav. of atmospheric air at $100^{\circ} = 1000$, that of aqueous vapor in its greatest state of compression for the temperature will be as follows:—

| Temperature. | | Specific Gravity. | Weight of 100 Cubic Inches. |
|--------------|-----|-------------------|-----------------------------|
| C. | F. | | |
| 0 | 32 | 5.690 | 0.136 grains. |
| 10 | 50 | 10.293 | 0.247 " |
| 15.5 | 60 | 14.108 | 0.338 " |
| 37.7 | 100 | 46.500 | 1.113 " |
| 65.5 | 150 | 170.293 | 4.076 " |
| 100 | 212 | 625.000 | 14.962 " |

The last number was experimentally found by Gay-Lussac; the others are calculated from that by the aid of Dalton's table of tensions, on the assumption that steam, not in a state of saturation, that is below the point of greatest density, obeys Boyle's law (which is, however, only approximately true), and that when it is cooled it contracts like the permanent gases.

Fig. 29.



Thus, there are two distinct methods by which a vapor may be reduced to the liquid form—*pressure*, by causing increase of density until the point of maximum density for a given temperature is reached; and *cold*, by which the point of maximum density is itself lowered. The most powerful effects are produced when both are conjoined.

For example, if 100 cubic inches of vapor of water at 37.7°C . (100°F .), in the state above described, had its temperature reduced to 10°C . (50°F .), not less than 0.89* grain of liquid water would necessarily separate, or very nearly eight-tenths of the whole.

Evaporation into a space filled with air or gas follows the same law as evaporation into a vacuum; as much vapor rises, and the condition of maximum density is assumed in the same manner, as if the space were perfectly empty; the sole difference lies in the length of time required. When a liquid evaporates into a vacuum, the point of greatest density is attained at once, while in the other case some time elapses before this happens; the particles of air appear to oppose a sort of mechanical resistance to the rise of the vapor. The ultimate effect is, however, precisely the same.

When to a quantity of perfectly dry gas confined in a vessel closed by mercury, a little water is added, the latter immediately begins to evaporate, and after some time as much vapor will be found to have risen from it as if no gas had been present, the quantity depending entirely on the temperature to which the whole is subjected. The tension of this vapor will add itself to that of the gas, and produce an expansion of volume, which will be indicated by an alteration of level in the mercury.

Vapor of water exists in the atmosphere at all times, and in all situations, and there plays a most important part in the economy of nature. The proportion of aqueous vapor present in the air is subject to great variation, and it often becomes important to determine its quantity. This is easily done by the aid of the foregoing principles.

Dew-point.—If the aqueous vapor be in its condition of greatest possible density for the temperature, or, as it is frequently but most incorrectly expressed, the air be saturated with vapor of water, the slightest reduction of temperature will cause the deposition of a portion in the liquid form. If, on the contrary, as is almost always in reality the case, the vapor of water be *below* its state of maximum density, that is, in an expanded condition, it is clear that a considerable fall of temperature may occur before liquefaction commences. The degree at which this takes place is called the dew-point, and it is determined with great facility by a very simple method. A little cup of thin tin-plate or silver, well polished, is filled with water of the temperature of the air, and a delicate thermometer is inserted. The water is then cooled by dropping in fragments of ice, or dissolving in it powdered sal-ammoniac, until moisture begins to make its appearance on the outside, dimming the bright metallic surface. The temperature of the dew-point is then read off upon the thermometer, and compared with that of the air.

Suppose, by way of example, that the latter were 21.1°C . (70°F .), and the dew-point 10°C . (50°F .), the elasticity of the watery vapor present would correspond to a maximum density proper to 10°C . (50°F .), and would support a column of mercury 0.375 inch high. If the barometer on the spot stood at 30 inches, therefore, 29.625 inches would be supported by the pressure of the dry air, and the remaining 0.375 inch by the vapor. Now, a cubic foot of such a mixture must be looked upon as made up of a cubic foot of dry air, and a cubic foot of watery vapor, occupying the same

* 100 cub. inch. aqueous vapor at 100°F . weighing 1.113 grain, would at 50°F . become reduced to 91.07 cub. inch., weighing 0.225 grain.

space, and having tensions indicated by the numbers just mentioned. A cubic foot, or 1728 cubic inches, of vapor at 70° F. would become reduced by contraction, according to the usual law, to 1662.8 cubic inches at 50° F.; this vapor would be at its maximum density, having the specific gravity pointed out in the table; hence, 1662.8 cubic inches would weigh 4.11 grains. The weight of the aqueous vapor contained in a cubic foot of air will thus be ascertained. In this country the difference between the temperature of the air and the dew-point seldom reaches 16.6° C. (30° F.); but in the Desert, with a temperature of 32.2° C. (90° F.), the dew-point sinks as low as -1.7° C. (29° F.), making the degrees of dryness 33.9° C. (61° F.).^o

Liquefaction of Gases.—The perfect resemblance in every respect which vapors bear to permanent gases, led, very naturally, to the idea that the latter might, by the application of suitable means, be made to assume the liquid state, and this surmise has been verified to a great extent by the experiments of Faraday. Out of the small number of such substances tried, no fewer than eight gave way; and it is quite fair to infer that, had means of sufficient power been at hand, the rest would have shared the same fate, and proved to be nothing more than the vapors of volatile liquids in a state very far removed from that of their maximum density. The subjoined table represents the results of Faraday's first investigations, with the pressure in atmospheres, and the temperatures at which the condensation takes place.

| | Atmospheres. | Temperatures.
C. | F. |
|-----------------------------|--------------|---------------------|--------------|
| Sulphur dioxide | 2 | 7.2° | 45° |
| Hydrogen sulphide | 17 | 10 | 50 |
| Carbon dioxide | 36 | 0 | 32 |
| Chlorine | 4 | 15.5 | 60 |
| Nitrogen monoxide | 50 | 7.2 | 45 |
| Cyanogen | 3.6 | 7.2 | 45 |
| Ammonia | 6.5 | 10 | 50 |
| Hydrochloric acid | 40 | 10 | 50 |

The method of proceeding was very simple: the materials were sealed up in a strong narrow tube, together with a little pressure-gauge, consisting of a slender tube closed at one end, and having within it, near the open extremity, a globule of mercury. The gas being disengaged by heat, accumulated in the tube, and by its own pressure brought about condensation. The force required for this purpose was judged of by the diminution of volume of the air in the gauge.

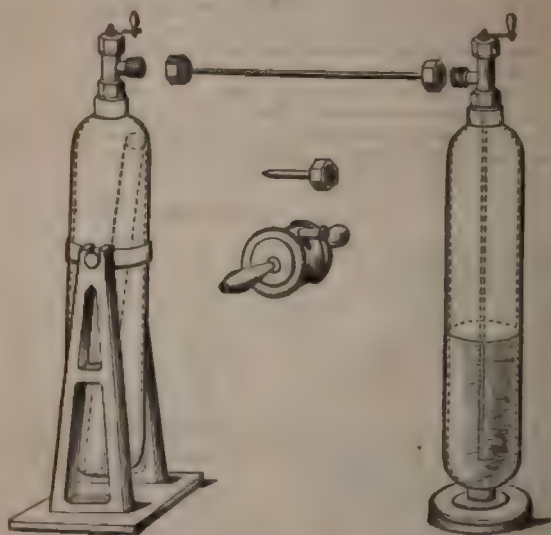
Fig. 30.



By the use of narrow green glass tubes of great strength, powerful condensing syringes, and an extremely low temperature, produced by means of the presently described, olefant gas, hydriodic and hydrobromic acids, phosphoretted hydrogen, and the gaseous fluorides of silicon and boron were successively liquefied. Oxygen, hydrogen, nitrogen, nitrogen dioxide, carbon monoxide, and marsh gas, refused to liquefy even at -110° C. (-146° F.) while subjected to pressures varying from 27 to 58 atmospheres. For beamhard Brunel, and, more recently, M. Thilorier, of Paris, succeeded in obtaining liquid carbon dioxide (commonly called carbonic acid) in great abundance. Thilorier's apparatus (fig. 31) consists of a pair of

extremely strong metallic vessels, one of which is destined to serve the purpose of a retort, and the other that of a receiver. They are made either of thick cast-iron or gun-metal, or, still better, of the best and heaviest boiler-plate, and are furnished with stop-cocks of a peculiar kind, the workmanship of which must be excellent. The generating vessel or retort has a pair of trunnions upon which it swings in an iron frame. The joints are secured by collars of lead, and every precaution is taken to prevent leakage under the enormous pressure the vessel has to bear. The receiver resembles the retort in every respect; it has a similar stop-cock, and is connected with the retort by a strong copper tube and a pair of union screw-joints; a tube passes from the stop-cock downwards, and terminates near the bottom of the vessel.

Fig. 31.



The operation is thus conducted: 2½ lb. of acid sodium carbonate, and 6½ lb. of water at 38° C. (100.4 F.), are introduced into the generator; oil of vitriol to the amount of 1½ lb. is poured into a copper cylindrical vessel, which is lowered down into the mixture, and set upright; the stop-cock is then screwed into its place, and forced home by a spanner and mallet. The machine is next tilted up on its trunnions, that the acid may run out of the cylinder and mix with the other contents of the generator; and this mixture is favored by swinging the whole backwards and forwards for a few minutes, after which it may be suffered to remain a little time at rest.

The receiver, surrounded with ice, is next connected with the generator, and both cocks are opened; the liquified carbon dioxide distils over into the colder vessel, and there again in part condenses. The cocks are now closed, the vessel is disconnected, the cock of the generator opened to allow the contained gas to escape, and, lastly, when the foam of gas has quite ceased, the stopcock itself is unscrewed, and the sodium sulphate turned out. This operation must be repeated five or six times before any con-

considerable quantity of liquefied carbon dioxide will have accumulated in the receiver. When the receiver thus charged has its stopcock opened, a stream of the liquid is forcibly driven up the tube by the elasticity of the gas contained in the upper part of the vessel.

The experimenter incurs great personal danger in using this apparatus, unless the utmost care be taken in its management. A dreadful accident occurred in Paris by the bursting of one of the iron vessels.

Liquid carbon dioxide is also very frequently prepared by means of an apparatus constructed by Natterer, of Vienna, which enables the experimentalist to work with less risk. The gas, disengaged by means of sulphuric acid from acid potassium carbonate, is pumped by means of a force-pump into a wrought-iron vessel, exactly as the air is pumped into the receiver of an air-gun. When a certain pressure has been reached, the gas is liquefied, and if the pressure be continued considerable quantities of the liquid carbon dioxide may be thus obtained. By this apparatus, nitrous oxide has been condensed to a liquid without the use of frigorific mixtures.

Complete Vaporization of Liquids under Great Pressures.—When the temperature of a liquid is raised sufficiently high, vaporization occurs under the highest pressure to which the substance can be subjected. Alcohol, ether, or rock oil, inclosed in a tube of strong glass or iron, is completely converted into vapor, only when the space not occupied by the liquid is somewhat greater than the volume of the liquid itself. With rock oil the empty space may be somewhat smaller than with alcohol, and with ether still less. Alcohol when thus heated acquires increased mobility, expands to twice its original volume, and is then suddenly converted into vapor. This change takes place at 207° C. (404.6° F.), when the alcohol occupies just half the volume of the tube; if the tube is more than half filled with alcohol, it bursts when heated. A glass tube one-third filled with water becomes opaque when heated, and bursts after a few seconds. If this chemical action of the water on the glass be diminished by the addition of a little carbonate of soda, the transparency of the glass will be much less impaired; and if the space occupied by the water be $\frac{1}{4}$ of the whole tube, the liquid will be converted into vapor at about the temperature of melting zinc. These observations were made by Cagniard de Latour in 1822.

In like manner Dr. Andrews has observed that, when liquid carbon dioxide is gradually heated in a sealed tube to 31° , the surface of demarcation between the liquid and gas becomes fainter, loses its curvature, and at last disappears. The space is then occupied by a homogeneous fluid, which exhibits, when the pressure is suddenly diminished, or the temperature slightly lowered, a peculiar appearance of moving or flickering stars throughout its entire mass. At temperatures above 31° no apparent liquefaction of carbon dioxide or separation into two distinct forms of matter can be effected, even under a pressure of 300 or 400 atmospheres. Similar results are obtained with nitrous oxide.

It appears indeed that there exists for every liquid a temperature, called by Andrews the "critical point," above which no amount of pressure is sufficient to retain it in the liquid form; it is therefore not surprising that very pressure, however intense, should fail to liquefy many bodies which usually exist in the form of gas.

Under the enormous pressures to which gases can be thus subjected, without liquefaction, they are found to deviate greatly from the laws of Boyle and Gay Lussac (pp. 45, 48). Andrews has recently found that carbon dioxide, at 60.7° under a pressure of 223 atmospheres, is reduced to $\frac{1}{2}$ of its original volume, or to less than one-half the volume it should occupy if it contracted according to Boyle's law. The coefficient of expansion of the same gas by heat increases rapidly with the pressure; between

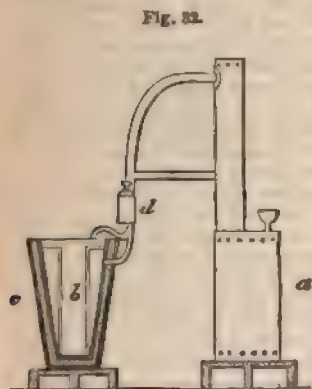
60° and 64° it is $1\frac{1}{2}$ times as great under 22 atmospheres, and more than 2½ times as great at 40 atmospheres, as at the pressure of 1 atmosphere.*

Cold produced by Evaporation.—This effect has been already adverted to: it arises from the conversion of sensible heat into latent by the rising vapor, and may be illustrated in a variety of ways. Ether dropped on the hand produces the sensation of great cold; and water contained in a thin glass tube, surrounded by a bit of rag, is speedily frozen when the rag is kept wetted with ether.

Ice-making machines and refrigerators are constructed on this principle. Harrison's apparatus for freezing water consists of a multitubular boiler containing about 10 gallons of ether and immersed in a trough of salt water. The boiler is connected with an exhausting pump, by the working of which the ether is rapidly volatilized, thereby cooling the boiler and the salt water surrounding it to about -4.45°C . (24°F). This cold water is made to flow through a channel in which are placed a number of vessels containing the water to be frozen, and when its temperature has been thus raised to about 28°F ., it is pumped back again into the trough containing the boiler, and then again cooled by the evaporation of the ether. In this manner a constant supply of cold salt water is kept up. The ether which is

evaporated is condensed in a worm surrounded by cold water, and returned with very little loss to the boiler.†

A simpler freezing apparatus is that of Carré, in which cold is produced by the rapid evaporation of liquefied ammonia gas. It consists essentially of a cylindrical boiler *a*, fig. 32, holding about two gallons, filled to about three-fourths of its capacity with a strong aqueous solution of ammonia, and connected by pipes with a wrought-iron annular condenser or freezer *c*. The boiler is first placed in a furnace, and the freezer in water cooled to 12°C . (53.6°F). The boiler is heated to 130°C . (266°F), whereupon ammonia gas is given off, and condenses in the freezer, together with about one-tenth of its own weight of water. This operation being completed, the boiler is removed from the



fire and immersed in cold water; the freezer, wrapped in very dry flannel, is placed outside, and the vessel containing the water to be frozen is placed in the cylindrical space *b*. As the boiler cools, the ammonia gas with which it is filled is redissolved, and the pressure being thus diminished, the ammonia which has been liquefied in *c* is again volatilized, and passes over towards *a*, to redissolve in the water which has remained in the boiler. This rapid evaporation of the ammonia causes a great absorption of heat, whereby the vessel *c* is reduced to a very low temperature, and the water contained in it frozen. To obtain better contact between the sides of the vessel *b* and the freezer, alcohol is poured between them. This apparatus gives about 4 lb. of ice in an hour at a price of about a farthing a pound; but large continuously working apparatus have been constructed which produce as much as 800 lb. of ice an hour.‡

* *Journal of the Chemical Society*, 1876, vol. II. p. 162.

† A figure of this apparatus is given in the *Pharmaceutical Journal*, vol. xvi. p. 477.

‡ See *Richardson and Watts's Chemical Technology*, part v. p. 286.

Water may also be frozen by the cold resulting from its own evaporation. When a little water is put into a watch-glass, supported by a triangle of glass over a shallow glass dish of sulphuric acid placed on the plate of an air-pump, the whole covered with a low receiver, and the air withdrawn as perfectly as possible, the water is in a few minutes converted into a thinness of ice. The absence of the air, and the rapid absorption of watery vapor by the acid, induce such quick evaporation that the water has its temperature almost immediately reduced to the freezing point.

The same apparatus is constantly used in the laboratory for drying substances which cannot bear heating without decomposition. Frequently also the air-pump is dispensed with, and the substance to be dried is simply placed over a vessel containing strong sulphuric acid, quicklime, or some other substance which absorbs moisture very rapidly, and covered over with a bell jar. Such an apparatus, with or without the air-pump, is called an *Exsiccator*.

All means of producing artificial cold yield, however, in intensity to that derived from the evaporation of the liquefied carbon dioxide just mentioned. When a jet of that liquid is allowed to issue into the air from a narrow aperture, so intense a degree of cold is produced by the vaporization of a part, that the remainder freezes to a solid, and falls in a shower of snow. By confining this jet of liquid to flow into the metal box shown in fig. 31, a large quantity of the solid oxide may be obtained; it closely resembles snow in appearance, and when held in the hand occasions a painful sensation of cold, while it gradually disappears. When it is mixed with a little ether, and poured upon a mass of mercury, the latter is almost instantly frozen, and in this way pounds of the solidified metal may be obtained. The addition of the ether facilitates the contact of the carbon dioxide with the mercury.

The temperature of a mixture of solid carbon dioxide and ether in the air, measured by a spirit-thermometer, was found to be -76.7°C . (-106°F). when the same mixture was placed beneath the receiver of an air-pump, and exhaustion rapidly made, the temperature sank to -110°C . (-166°F). This was the method of obtaining extreme cold employed by Faraday in his last experiments on the liquefaction of gases. Under such circumstances, the liquefied hydriodic and hydrobromic acids, sulphur dioxide, carbon dioxide, nitrogen monoxide, hydrogen sulphide, cyanogen, and ammonia, froze to colorless transparent solids, and alcohol became thick and oily.

Determination of the Specific Gravity of Gases and Vapors.

To determine the specific gravity of a gas, a large glass globe is filled with the gas to be examined, in a perfectly pure and dry state, having a known temperature, and an elastic force equal to that of the atmosphere at the time of the experiment. The globe so filled is weighed. It is then exhausted at the air-pump so far as possible, and again weighed. Lastly, it is filled with dry air, the temperature and pressure of which are known, and its weight once more determined. On the supposition that the temperature and elasticity are the same in both cases, the specific gravity is at once obtained by dividing the weight of the gas by that of the air.

The globe or flask must be made very thin, and fitted with a brass cap, surmounted by a small but excellent stopcock. A delicate thermometer

Fig 33.



should be placed in the inside of the globe, secured to the cap. The gas must be generated at the moment, and conducted at once into the previously exhausted vessel, through a long tube filled with fragments of pumice moistened with oil of vitriol, or some other extremely hygroscopic substance, by which it is freed from all moisture. As the gas is necessarily generated under some pressure, the elasticity of that contained in the filled globe will slightly exceed the pressure of the atmosphere, and this is an advantage, since, by opening the stopcock for a single instant, when the globe has attained an equilibrium of temperature, the tension becomes exactly that of the air, so that all barometrical correction is avoided, unless the pressure of the atmosphere should sensibly vary during the time occupied by the experiment. It is hardly necessary to observe that the greatest care must also be taken to purify and dry the air used as the standard of comparison, and to bring both gas and air as nearly as possible to the same temperature, so as to obviate the necessity of a correction, or at least to reduce almost to nothing the errors involved by such a process.

VAPORS.—1. *Dumas's Method.* This method consists in determining the weight of a given volume of the vapor at a known pressure and temperature.

Fig. 34.



A large glass globe about three inches in diameter is taken, and its neck softened and drawn out in the blowpipe flame, as represented in fig. 34; this is accurately weighed. About 100 grains of the volatile liquid are then introduced, by gently warming the globe and dipping the point into the liquid, which is then forced upwards by the pressure of the air as the vessel cools. The globe is next firmly attached by wire to a handle, in such a manner that it may be plunged into a bath of boiling water or heated oil, and steadily held with the point projecting upwards. The bath must have a temperature considerably above that of the boiling point of the liquid. The latter becomes rapidly converted into vapor, which escapes by the narrow orifice, chasing before it the air of the globe. When the issue of vapor has wholly ceased, and the temperature of the bath appears nearly uniform, the open extremity of the point is hermetically sealed by a small blowpipe flame. The globe

is removed from the bath, suffered to cool, cleansed if necessary, and weighed, after which the neck is broken off beneath the surface of water which has been boiled and cooled out of contact of air, or (better) under mercury. The liquid enters the globe, and, if the expulsion of the air by the vapor has been complete, fills it; if otherwise, an air-bubble is left, whose volume can be easily ascertained by pouring the liquid from the globe into a graduated jar, and then refilling the globe, and repeating the same observation. The capacity of the vessel is thus at the same time known; and these are all the data required.* An example will render the whole intelligible.

* Messrs. Playfair and Wanklyn have described an important modification of this process, whereby the densities of a vapor at temperatures below the boiling point of the liquid may be determined. This object is attained by mixing the vapor of the body with a measured volume of a permanent gas—hydrogen, for instance.—*Journ. of the Chem. Soc.* vol. xv. p. 143.

Determination of the Vapor-density of Acetone.

| | |
|---|---------------------|
| Capacity of globe | 31.61 cubic inches. |
| Weight of globe filled with dry air at
45° F. and 30.24 inches barometer . . . | 2070.88 grains. |
| Weight of globe filled with vapor at
212° F., temp. of the bath at the
moment of sealing the point, and
30.24 inches barometer | 2076.81 grains. |
| Residual air, at 45° F. and 30.24
inches barometer | 0.60 cubic inches. |

31.61 cubic inches of air at 52° and 30.24 in. bar. = 32.36 cub. inches at
60° F. and 30 inch. bar., weighing 10.035 grains.
Hence, weight of empty globe, 2070.88 — 10.035 = 2060.845 grains.

0.6 cubic inch of air at 45° = 0.8 cub. inch at 212°; weight of do. by cal-
culation = 0.191 grain.

31.61 — 0.8 = 30.81 cubic inches of vapor at 212° and 30.24 in. bar.,
which, on the supposition that it would bear cooling to 60° without liquefaction,
would, at that temperature, and under a pressure of 30 inch. bar., be-
come reduced to 24.18 cubic inches.

Balance—

| | |
|-------------------------------------|------------------|
| Weight of globe and vapor | 2076.810 grains. |
| “ residual air | 0.191 “ |
| | <hr/> |
| Weight of globe | 2076.619 “ |
| | <hr/> |
| Weight of globe | 2060.845 “ |

Weight of the 24.18 cubic inches of vapor 15.774 “

Consequently, 100 cubic inches of such vapor must
weigh 65.23 “

100 cubic inches of air, under similar circumstances,
weigh 31.01 “

$\frac{65.23}{31.01} = 2.103$, the specific gravity of the vapor in question, that of air
being unity.

Or, the weight of 100 cubic inches of hydrogen being 2.147 grains,

$\frac{65.23}{2.147} = 30.35$ is the specific gravity of acetone vapor referred to hydrogen
as unity.

This vapor-density (D) may also be readily calculated by means of the
formula:—

$$D = \frac{P + Vn_1}{(V - v)n'_1}$$

P = difference of weight (in grams) between the globe filled with air
and when filled with vapor.

V = capacity of globe in cubic centimetres.

n_1 = weight of one cubic centimetre of air at the temperature at which
the globe filled with air was weighed.

n'_1 = weight of one cubic centimetre of air at the temperature of sealing
the globe.

The values of n_1 and n'_1 (in grams) for each degree centigrade from 0 to
300° are given in the Appendix, Table VII.

In very exact experiments, account must be taken of the change of capacity of the glass globe by the high temperature of the bath. When this correction is neglected, the density of the vapor will come out a little too high. The error of the mercurial thermometer at high temperatures is, however, in the opposite direction.

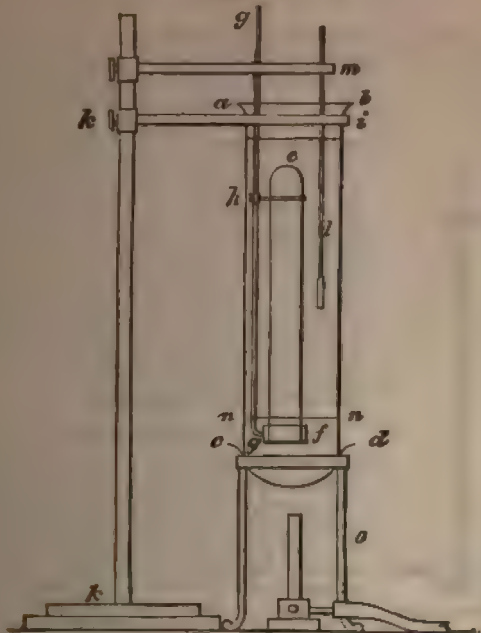
The preceding method is applicable to the determination of the vapor-densities of all substances whose boiling points are within the range of the mercurial thermometer, that is to say, not exceeding 300°C ., and therefore to nearly all volatile organic compounds; indeed, there are but few such compounds which can bear higher temperatures without decomposition. But for mineral substances, such as sulphur, iodine, volatile metallic chlorides, etc., it is often necessary to employ much higher temperatures; and for such cases a modification of the process has been devised by Deville and Troost. It consists in using a globe of porcelain instead of glass, heating it in the vapor of a substance whose boiling point is known and constant, and sealing the globe by the flame of the oxy-hydrogen blowpipe. The vapors employed for this purpose are those of mercury, which boils at 350°C .; of sulphur, which boils at 440° ; of cadmium, boiling at 800° ; and of zinc, boiling at 1040° . The use of these liquids of constant boiling point obviates the necessity of determining the temperature in each experiment, which at such degrees of heat would be very difficult.

2. Gay-Lussac's Method.—This method consists in ascertaining the volume occupied by a given weight of a substance when converted into vapor at a known temperature and pressure. For this purpose a small bulb of very thin glass with a capillary neck is weighed, filled with the liquid, sealed, and again weighed, the difference of the two weighings of course giving the weight of the liquid. It is then introduced into a graduated glass jar filled with mercury, inverted in a basin of mercury, and immersed in a bath of water or oil, and heat is applied to the bath till the bulb bursts, and the liquid is converted into vapor, which depresses the mercury in the gas-jar to a certain level. This is read off, together with the temperature of the bath and the height of the barometer, and from these readings the volume of the vapor at a certain pressure and temperature. A convenient apparatus for the purpose is represented in figure 35. It consists of a cylinder of rather thin glass, *a b c d*, in shape like a very large test-tube, about 16 or 18 inches long, and 5 or 6 in diameter. At the lower and closed end it is rounded, and care must be taken that it is thin enough to stand the application of heat, and yet strong enough to bear the weight of the mercury and the rest of the apparatus which will have to be inserted. A small and rather light gas-jar *e*, divided into inches or half cubic centimetres, is supported at its lower end by an iron cup *f*, attached to a rod *g g* of the same metal. In the engraving it is represented in the act of being lowered into its place. The upper end of the jar is kept steady by the ring *h*, which slides on the rod *g g*. The cylinder is retained in its vertical position by the ring *i* sliding on the massive retort-stand *k k*. The rod *g g* and the thermometer *l* are supported by the arm *m*, also attached to the retort-stand. The cylinder being charged up to the line *n n* with mercury, the gas-jar *e*, filled with mercury, and having the glass bulb containing the liquid to be examined inserted, is placed in the position seen in the figure. The cylinder is then to be filled with water, or neat's-foot oil, until the gas-jar is covered for at least an inch. The cylinder may be supported on wire-gauze over the tripod *a*, or in any other convenient manner. Heat may be applied by means of a Bunsen's burner.

Great care must be taken, in passing the bulb up into the gas-jar, to prevent fracture. The most convenient way of accomplishing this, is to place the lower end of the jar in a mercurial trough, and to incline it to

at an angle of about 45° . The bulb is then to be held between the thumb and first two fingers, the tail towards the palm of the hand; it is then presented to the opening of the gas-jar, and when inserted is to be held so that the bulb will then ascend to the top.

Fig. 36.



To determine the elastic force of the vapor, the height of the column of water or oil must be noted and reduced by calculation to the corresponding value in millimetres of mercury. The elastic force P of the vapor is then found by adding this number to the height of the barometer, and deducting the height of the mercury in the gas-jar above that in the outer cylinder.

By this mode of proceeding we ascertain the volume which a known weight W' of substance occupies at a given temperature and pressure, and all that remains to determine the weight W of the same volume V of air at the same temperature T and pressure P . This is given in grams by the formula—

$$W = 0.0012932 V \cdot \frac{1}{1 + 0.00367 T} \cdot \frac{P}{760}$$

The value of the expression $\frac{1}{1 + 0.00367 T}$ have been calculated by

C. Grisille Williams for all temperatures from 10° to 150° C. (see Table VIII. in the Appendix); and dividing the weight W' of the vapor by these values, we obtain, for the density, the expression—

$$D = \frac{W'}{W} = W' \frac{1 + 0.00367 T}{0.0012932 V} \cdot \frac{760}{P}.$$

If the gas-jar is graduated in cubic inches and the weights are grains, the expression becomes—

$$D = W' \frac{1 + 0.00367 T}{0.31 V} \cdot \frac{760}{P}.$$

Of the two methods of determining vapor densities above described, Dumas has the advantage in simplicity of apparatus and fac-

Fig. 35.



execution, especially for high temperatures. Indeed, for temperatures above 150° it is the one that can be employed; but it requires a substance, and does not permit of the being determined at more than one temperature without making a separate experiment in each case. The process of Gay-Lussac, on the other hand, permits numerous experiments with small specimens of substance at any desired temperature within certain ranges, and thus enables an operator, in a very short time, to accumulate information regarding certain physical properties of substances which it is often very desirable to obtain—such, for example, as the lowest temperature at which the substance under study begins to volatilize, or the laws of permanent gases.

3. *Hofmann's Method.*—This is a modified Gay-Lussac's method, devised by Dr. A. W. Hofmann (*Deut. Chem. Ges. Ber.* 1868, p. 198) for determining the vapor-densities of high-boiling liquids at reduced pressure, and therefore at comparatively low temperatures. A graduated glass tube, a metre long and 15 to 20 mm. wide, is filled with mercury and inverted in the little cup A, where a barometric vacuum 20 to 30 mm. high is maintained at the top. The long tube is inclosed in a shorter tube 30 to 40 mm. wide and 80 to 90 mm.

drawn out at the top to a conducting tube of moderate width, which is bent at right angles, and connected with a glass or copper vessel in which water, aniline, or other liquid can be boiled. The lower part of the inner tube is widened and rests upon a large cork, through which passes an escape-tube T. By this arrangement, a stream of vapor of water, or other volatile liquid can be made to pass through the space between the two tubes, so as to keep the upper part of the barometer-tube at the temperature required for the determination. The substance whose vapor-density is to be determined, is introduced into the barometric vacuum through small glass tubes fitted with ground stoppers, which are forced into the tube under the tension of the vapor. The great advantage of this method is that it enables determinations to be made at comparatively low temperatures. Thus, in the case of liquids boiling under the ordinary pressure at 120° or even 150°, the vapor-density may be accurately determined at the temperature of water.

Sources of Heat.

The first and greatest source of heat, compared with which all others are totally insignificant, is the sun. The luminous rays are accompanied by heat-rays, which, striking against the surface of the earth, raise its temperature; this heat is communicated to the air by convection, as already described, air and gases in general not being sensibly heated by the passage of the rays.

A second source of heat is supposed to exist in the interior of the earth. It has been observed that, in sinking mine-shafts, boring for water, etc., the temperature rises, in descending, at the rate, it is said, of about 1°C . (1.8°F .) for every 45 feet, or 65°C . (117°F .) per mile. On the supposition that the rise continues at the same rate, the earth, at the depth of less than two miles, would have the temperature of boiling water; at nine miles, it would be red-hot; and at thirty or forty miles depth, all known substances would be in a state of fusion.*

According to this idea, the earth must be looked upon as an intensely heated fluid spheroid, covered with a crust of solid badly conducting matter, cooled by radiation into space, and bearing somewhat the same proportion in thickness to the ignited liquid within, that the shell of an egg bears to its fluid contents. Without venturing to offer any opinion on this theory, it may be sufficient to observe that it is not positively at variance with any known fact, that the figure of the earth is really such as would be assumed by a fluid mass; and, lastly, that it offers the best explanation we have of the phenomena of hot springs and volcanic eruptions, and agrees with the chemical nature of their products.

Among the other sources of heat are chemical combination and mechanical work.

The disengagement of heat in the act of combination is a phenomenon of the utmost generality. The quantity of heat given out in each particular case is fixed and definite; its intensity is dependent upon the time over which the action is extended. Many admirable researches on this subject have been published; but their results will be more advantageously considered at a later part of this work, in connection with the laws of chemical combination.

Heat produced by Mechanical Work.—Heat and motion are convertible one into the other. The powerful mechanical effects produced by the elasticity of the vapor evolved from heated liquids afford abundant illustration of the conversion of heat into motion; and the production of heat by friction, by the hammering of metals, and in the condensation of gases (p. 52), shows with equal clearness that motion may be converted into heat.

In some cases the rise of temperature thus produced appears to be due to a diminution of heat capacity in the body operated upon, as in the case of a compressed gas just alluded to. Malleable metals, also, as iron and copper, which become heated by hammering or powerful pressure, are found thereby to have their density sensibly increased, and their capacity of heat diminished. A soft iron nail may be made red hot by a few dexterous blows on an anvil; but the experiment cannot be repeated until the metal has been annealed, and in that manner restored to its former physical state.

But the amount of heat which can be developed by mechanical force is,

* The Artesian well at Grenelle, near Paris, has a depth of 1774.5 English feet; it is bored through the chalk basin to the sand beneath. The temperature of the water, which is exceedingly abundant, is 82°F .; the mean temperature of Paris is 54°F .; the difference is 28°F ., which gives a rate of about 1° for 53 feet.

in most cases, out of all proportion to what can be accounted for in this way. Sir H. Davy melted two pieces of ice by rubbing them together in a vacuum at the temperature of 0° ; and Count Rumford found that the heat developed by the boring of a brass cannon was sufficient to bring to the boiling point two and a half gallons of water, while the dust or shavings of metal cut by the borer weighed only a few ounces. In these and all similar cases the heat appears as a direct result of the force expended; the motion is converted into heat.

The connection between heat and mechanical force appears still more intimate when it is shown that they are related by an exact numerical law, a given quantity of the one being always convertible into a definite amount of the other. The first approximate determination of this most important numerical relation was made by Count Rumford in the manner just alluded to. A brass cylinder inclosed in a box containing a known weight of water at 60° F. was bored by a steel borer made to revolve by horse power, and the time was noted which elapsed before the water was raised to the boiling point by the heat resulting from the friction. In this manner it was found that the heat required to raise the temperature of a pound of water by 1° F. is equivalent to 103.4 times the force expended in raising a pound weight one foot high, or to 1934 "foot-pounds," as it is technically expressed. This estimate is now known to be too high, no account having been taken of the heat communicated to the containing vessel, or of that which was lost by dispersion during the experiment.

For the most exact determinations of the mechanical equivalent of heat we are indebted to the careful and elaborate researches of Dr. J. P. Joule. From experiments made in the years 1840-43 on the relations between the heat and mechanical power generated by the electric current, Dr. Joule was led to conclude that the heat required to raise the temperature of a pound of water 1° F. is equivalent to 838 foot-pounds. This he afterwards reduced to 772; and a nearly equal result was afterwards obtained by experiments on the condensation and rarefaction of gases; but this estimate has since been found to be likewise too great.

The most trustworthy results are obtained by measuring the quantity of heat generated by the friction between solids and liquids. It was for a long time believed that no heat was evolved by the friction of liquids and gases; but in 1842 Meyer showed that the temperature of water may be raised 22° or 23° F. by agitating it. The warmth of the sea after a few days of stormy weather is also probably an effect of fluid friction.

The apparatus employed by Dr. Joule for the determination of this important constant, by means of the friction of water, consisted of a brass

Fig. 37.



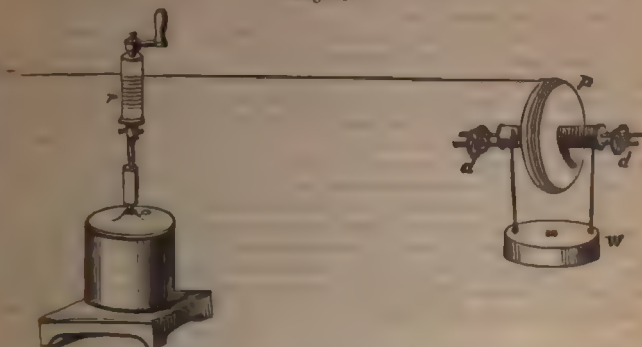
Fig. 38.



paddle-wheel furnished with eight sets of revolving vanes, working between four sets of stationary vanes. This revolving apparatus, of which fig. 37 shows a horizontal, and fig. 38 a vertical section, was firmly fitted into a copper vessel (see fig. 39) containing water, in the lid of which were two necks, one for the axis to revolve in without touching, the other for the insertion of a thermometer. A similar apparatus, but made of iron, and of smaller size, having six rotatory and eight sets of stationary vanes, was used for the experiments on the friction of mercury. The apparatus for the friction of cast-iron consisted of a vertical axis carrying a bevelled cast-iron wheel, against which a bevelled wheel was pressed

by a lever. The wheels were inclosed in a cast-iron vessel filled with mercury, the axis passing through the lid. In each apparatus motion was given to the axis by the descent of leaden weights *W* (fig. 39) suspended by strings from the axis of two wooden pulleys, one of which is shown at *p*, their axes being supported on friction wheels *d d*, and the

Fig. 39.



pulleys being connected by fine twine with a wooden roller *r*, which, by means of a pin, could be easily attached to or removed from the friction apparatus.

The mode of experimenting was as follows :—The temperature of the frictional apparatus having been ascertained, and the weights wound up, the roller was fixed to the axis, and the precise height of the weights ascertained; the roller was then set at liberty, and allowed to revolve till the weights touched the floor. The roller was then detached, the weights wound up again, and the friction renewed. This having been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the apartment was ascertained by observations made at the beginning, middle, and end of each experiment. Corrections were made for the effects of radiation and conduction; and, in the experiments with water, for the quantities of heat absorbed by the copper vessel and the paddle-wheel. In the experiments with mercury and cast-iron, the heat-capacity of the entire apparatus was ascertained by observing the heating effect which it produced on a known quantity of water in which it was immersed. In all the experiments, corrections were also made for the velocity with which the weights came to the ground, and for the friction and rigidity of the strings. The thermometers used were capable of indicating a variation of temperature as small as $\frac{1}{40}$ of a degree Fahrenheit.

The following table contains a summary of the results obtained by this method. The second column gives the results as they were obtained in air. In the third column the same results corrected for a vacuum :—

| Material employed. | Equivalent in air. | Equivalent in vacuum. | Mean. |
|--------------------|---------------------------------|---------------------------------|---------|
| Water . . . | 773.640 | 772.692 | 772.692 |
| Mercury . . . | { 773.762
776.303
776.997 | { 772.814
775.352
776.045 | 774.083 |
| Cast-iron . . . | { 774.880 | { 774.930 | 774.987 |

In the experiments with cast-iron, the friction of the wheels produced a considerable vibration of the framework of the apparatus, and a loud sound, it was therefore necessary to make allowance for the quantity of force expended in producing these effects. The number 772.692, obtained by the friction of water, is regarded as the most trustworthy; but even this may be a little too high; because even in the friction of fluids it is impossible entirely to avoid vibration and sound. The conclusions deduced from these experiments are—

1. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the force expended.*

2. *That the quantity of heat capable of increasing the temperature of 1 lb. of water (weighed in vacuo, and between 55° and 60°) by 1° F., requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lbs. through the space of 1 foot.*

Or, the heat capable of increasing the temperature of 1 gram of water by 1° C., is equivalent to a force represented by the fall of 423.65 grams through the space of 1 metre. This is consequently the effect of "a unit of heat."

Experiments made by other philosophers on the work done by a steam-engine, on the heat evolved by an electro-magnetic engine at rest and in motion, and on the heat evolved in the circuit of a voltaic battery and in a metallic wire through which an electric current is passing, have given values for the mechanical equivalent of heat very nearly equal to the above.

Dynamical Theory of Heat.

For a very long time two rival theories have been held regarding the nature of heat: on the one hand, heat has been viewed as having a material existence, though differing from ordinary matter in being without weight, and in other respects; on the other hand, it has been regarded as a state or condition of ordinary matter, and generally as a condition of motion. From the latter part of the last century, until the modern researches upon the mechanical equivalent, the former view had by far the greater number of adherents. Its popularity may be chiefly traced to the teaching of Black and Lavoisier. By the former of these philosophers, the various capacities for heat, or specific heats, of different bodies, seem to have been regarded as analogous to the various proportions of the same acid required to neutralize equal quantities of different bases, while the solid, liquid, and gaseous states were explained by Black as representing so many distinct proportions in which heat was capable of combining with ordinary matter. Very similar views were advocated by Lavoisier, he regarded all gases as compounds of a base characteristic of each, with caloric, and supposed that when, as the result of chemical action, they assumed the liquid or solid state, this caloric was set free, and appeared as sensible heat.

Heat was compared by these philosophers to a material substance, in order to explain its then known quantitative relations; and from this point of view the conception introduced by them had the great advantage of being more easily grasped than any which the advocates of the immaterial nature of heat had to offer in its place. It was much easier to conceive of definite quantities of an exceedingly subtle substance or fluid, than of definite quantities of motion, which was itself undefined as to its nature. It was a direct consequence of the material view, that heat should be considered as indestructible and as incapable of being produced, and therefore that the total quantity of heat in the universe should be regarded as at all times the same.

But, on the other hand, this hypothesis did not afford a satisfactory ex-

planation of the production of heat by mechanical means. Here it was not easy to deny the actual generation of heat, or to explain the effects as depending merely on its altered distribution. Nevertheless, the evolution of heat by friction and percussion was generally considered, by the advocates of the material view, as in some way resulting from a diminution in the capacities for heat of the bodies operated upon; and this explanation derived considerable support from the remark, made by Black, that a piece of red iron, which has been once made red hot by hammering (see p. 73), cannot be so heated a second time until it has been heated to redness in a fire and allowed to cool. In this case, certainly, it seemed as though the hammering forced out heat from the mass of iron, like water from a sponge, and that a fresh supply was taken up when the iron was put in the fire. This explanation, however, did not satisfy Rumford, who, in the investigation described above, made direct experiments upon the specific heat of the chips of metal detached by the friction, and found it to be identical with that of brass under ordinary circumstances. Still more decisive proof that the heat generated by friction cannot be ascribed to a diminution of specific heat in the substances operated on was afforded by Davy's experiment on the liquefaction of ice by friction; for in this case the ice was converted into a liquid having twice the specific heat of the ice itself. Hence Davy drew the conclusion that "the immediate cause of the phenomena of heat is motion, and the laws of its communication are precisely the same as the laws of the communication of motion."

The mechanical, or dynamical theory, which regarded heat as consisting in a state of molecular motion, cannot, however, be said to have been definitely established, until it also was made quantitative,—until it was shown that exact numerical laws regulate the production of heat by work or of work by heat, equally with its production during solidification and disappearance during fusion.

To illustrate the general nature of the dynamical theory of heat, we give an outline of the view of the constitution of gases, first put forward, in its present form, by Joule;† and subsequently developed by Krönig,‡ and Clausius,§ and of the explanation of the relation existing between solids, liquids, and gases, which has been deduced from it by the last-named philosopher.

First, then, it is assumed that the particles of all bodies are in constant motion, and that this motion constitutes heat, the kind and quantity of motion varying according to the state of the body, whether solid, liquid, or gaseous.

In gases, the molecules—each molecule being an aggregate of atoms—are supposed to be constantly moving forward in straight lines, and with a constant velocity, till they impinge against each other, or against an impenetrable wall. This constant impact of the molecules produces the expansive tendency or elasticity which is the peculiar characteristic of the gaseous state. The rectilinear movement is not, however, the only one with which the particles are affected. For the impact of two molecules, unless it takes place exactly in the line joining their centres of gravity, must give rise to a rotatory motion; and, moreover, the ultimate atoms of which the molecules are composed may be supposed to vibrate within certain limits, being, in fact, thrown into vibration by the impact of the molecules. This vibratory motion is called by Clausius, *the motion of the constituent atoms*. The total quantity of heat in the gas is made up of the progressive motion of the molecules, together with the vibratory and other

* Elements of Chemical Philosophy, 1812, pp. 64, 66.

† Ann. Ch. Phys. (3) i. 381.

‡ Pogg. Ann. xcix. 316.

§ Ibid. 333.

motions of the constituent atoms; but the progressive motion alone, which is the cause of the expansive tendency, determines the temperature. Now, the outward pressure exerted by the gas against the containing envelope arises, according to the hypothesis under consideration, from the impact of a great number of gaseous molecules against the sides of the vessel. But at any given temperature, that is, with any given velocity, the number of such impacts taking place in a given time must vary inversely as the volume of the given quantity of gas: hence the pressure varies inversely as the volume, or directly as the density, which is Boyle's law.

When the volume of the gas is constant, the pressure resulting from the impact of the molecules is proportional to the sum of the masses of all the molecules multiplied into the squares of their velocities; in other words, to the so-called *vis viva* or *working force* of the progressive motion. If, for example, the velocity be doubled, each molecule will strike the sides of the vessel with a twofold force, and its number of impacts in a given time will also be doubled: hence the total pressure will be quadrupled.

Now, we know that when a given quantity of any perfect gas is maintained at a constant volume, it tends to expand by $\frac{1}{273}$ of its bulk at zero for each degree centigrade. Hence the pressure or elastic force increases proportionally to the temperature reckoned from $-273^{\circ}\text{C}.$; that is to say, to the absolute temperature. Consequently, the absolute temperature is proportional to the working force of the progressive motion.

Moreover, as the motions of the constituent particles of a gas depend on the manner in which its atoms are united, it follows that in any given gas the different motions must be to one another in a constant ratio; and, therefore, the *vis viva* or *working force* of the progressive motion must be an aliquot part of the entire working force of the gas; hence also the absolute temperature is proportional to the total working force arising from all the motions of the particles of the gas.

From this it follows that the quantity of heat which must be added to a gas of constant volume in order to raise its temperature by a given amount, is constant and independent of the temperature. In other words, the specific heat of a gas referred to a given volume is constant, a result which agrees with the experiments of Regnault, mentioned at p. 52. This result may be otherwise expressed, as follows: *The total or working force of the gas is to the working force of the progressive motion of the molecules, which is the measure of the temperature, in a constant ratio.* This ratio is different for different gases, and is greater as the gas is more complex in its constitution; in other words, as its molecules are made up of a greater number of atoms. The specific heat referred to a constant pressure is known to differ from the true specific heat only by a constant quantity.

The relations just considered between the pressure, volume, and temperature of gases, presuppose, however, certain conditions of molecular constitution, which are, perhaps, never rigidly fulfilled: and, accordingly, the experiments of Magnus and Regnault show (pp. 49-50) that gases do exhibit slight deviations from Gay-Lussac and Boyle's laws. What the conditions are which strict adherence to these laws would require, will be better understood by considering the differences of molecular constitution which must exist in the solid, liquid, and gaseous states.

A movement of molecules must be supposed to exist in all three states. In the *solid state*, the motion is such that the molecules oscillate about certain positions of equilibrium, which they do not quit, unless they are acted upon by external forces. This vibratory motion may, however, be of a very complicated character. The constituent atoms of a molecule may vibrate separately, the entire molecules may also vibrate as such about their centres of gravity, and the vibrations may be either rectilinear

or rotatory. Moreover, when extraneous forces act upon the body as in shocks, the molecules may permanently alter their relative positions.

In the *liquid state*, the molecules have no determinate positions of equilibrium. They may rotate completely about their centres of gravity, and may also move forward into other positions. But the repulsive action arising from the motion is not strong enough to overcome the mutual attraction of the molecules, and separate them completely from each other. A molecule is not permanently associated with its neighbors, as in the solid state; it does not leave them spontaneously, but only under the influence of forces exerted upon it by other molecules, with which it then comes into the same relation as with the former. There exists, therefore, in the liquid state, a vibratory, rotatory, and progressive movement of the molecules, but so regulated that they are not thereby forced asunder, but remain within a certain volume without exerting any outward pressure.

In the *gaseous state*, on the other hand, the molecules are removed quite beyond the sphere of their mutual attractions, and travel onward in straight lines according to the ordinary laws of motion. When two such molecules meet, they fly apart from each other, for the most part with a velocity equal to that with which they came together. The perfection of the gaseous state, however, implies: 1. That the space actually occupied by the molecules of the gas be infinitely small in comparison with the entire volume of the gas; 2. That the time occupied in the impact of a molecule, either against another molecule or against the sides of the vessel, be infinitely small in comparison with the interval between any two impacts; 3. That the influence of the molecular forces be infinitely small. When these conditions are not completely fulfilled, the gas partakes more or less of the nature of a liquid, and exhibits certain deviations from Gay-Lussac and Boyle's laws. Such is, indeed, the case with all known gases; to a very slight extent with those which have not yet been reduced to the liquid state; but to a greater extent with vapors and condensable gases, especially near the points of condensation.

Let us now return to the consideration of the liquid state. It has been said that the molecule of a liquid, when it leaves those with which it is associated, ultimately takes up a similar position in regard to other molecules. This, however, does not preclude the existence of considerable irregularities in the actual movements. Now, at the surface of the liquid, it may happen that a particle, by a peculiar combination of the rectilinear, rotatory, and vibratory movements, may be projected from the neighboring molecules with such force as to throw it completely out of their sphere of action, before its projectile velocity can be annihilated by the attractive force which they exert upon it. The molecule will then be driven forward into the space above the liquid, as if it belonged to a gas, and that space, if originally empty, will, in consequence of the action just described, become more and more filled with these projected molecules, which will compact themselves within it exactly like a gas, impinging and exerting pressure upon the sides of the envelope. One of these sides, however, is formed by the surface of the liquid, and when a molecule impinges upon this surface, it will, in general, not be driven back, but retained by the attractive forces of the other molecules. A state of equilibrium, not static, but dynamic, will therefore be attained when the number of molecules projected in a given time into the space above is equal to the number which in the same time impinge upon and are retained by the surface of the liquid. This is the process of vaporization. The density of the vapor required to insure the compensation just mentioned, depends upon the rate at which the particles are projected from the surface of the liquid, and this again upon the *rapidity of their movement within the liquid*,

that is to say, upon the temperature. It is clear, therefore, that the density of a saturated vapor must increase with the temperature.

If the space above the liquid is previously filled with a gas, the molecules of this gas will impinge upon the surface of the liquid, and thereby exert pressure upon it; but as these gas-molecules occupy but an extremely small proportion of the space above the liquid, the particles of the liquid will be projected into that space almost as if it were empty. In the middle of the liquid, however, the external pressure of the gas acts in a different manner. There, also, it may happen that the molecules may be separated with such force as to produce a small vacuum in the midst of the liquid. But this space is surrounded on all sides by masses which afford no passage to the disturbed molecules; and in order that they may increase to a permanent vapor-bubble, the number of molecules projected from the inner surface of the vessel must be such as to produce a pressure outwards equal to the external pressure tending to compress the vapor-bubble. The boiling of the liquid will, therefore, be higher as the external pressure is greater.

According to this view of the process of vaporization, it is possible that vapor may rise from a solid as well as from a liquid; but it by no means necessarily follows that vapor must be formed from all bodies at all temperatures. The force which holds together the molecules of a body may be too great to be overcome by any combination of molecular movements, so long as the temperature does not exceed a certain limit.

The production and consumption of heat which accompany changes in the state of aggregation, or of the volume of bodies, are easily explained, according to the preceding principles, by taking account of the work done by the acting forces. This work is partly *external* to the body, partly *internal*. To consider first the *internal* work:

When the molecules of a body change their relative positions, the change may take place either in accordance with or in opposition to the action of the molecular forces existing within the body. In the former case, the molecules, during the passage from one state to the other, have a certain velocity imparted to them, which is immediately converted into heat; in the latter case, the velocity of their movement, and consequently the temperature of the body, is diminished. In the passage from the solid to the liquid state, the molecules, although not removed from the spheres of their mutual attractions, nevertheless change their relative positions in opposition to the molecular forces, which forces have, therefore, to be overcome. In evaporation, a certain number of the molecules are completely separated from the remainder, which again implies the overcoming of opposing forces. In both cases, therefore, work is done, and a certain portion of the working force of the molecules, that is, of the heat of the body, is lost. But when once the perfect gaseous state is attained, the molecular forces are completely overcome, and any further expansion may take place without internal work, and, therefore, without loss of heat, provided there is no external resistance.

But in nearly all cases of change of state or volume, there is a certain amount of external resistance to be overcome, and a corresponding loss of heat. When the pressure of a gas, that is to say, the impact of its atoms, is exerted against a movable obstacle, such as a piston, the molecules lose just as much of their moving power as they have imparted to the piston, and, consequently, their velocity is diminished and the temperature lowered. On the contrary, when a gas is compressed by the motion of a piston, its molecules are driven back with greater velocity than that with which they impinged on the piston, and, consequently, the temperature of the gas is raised.

When a liquid is converted into vapor, the molecules have to overcome the atmospheric pressure or other external resistance, and, in consequence of this, together with the internal work already spoken of, a large quantity of heat disappears, or is rendered *latent*, the quantity thus consumed being, to a considerable extent, affected by the external pressure. The liquefaction of a solid, not being attended with much increase of volume, involves but little external work; nevertheless the atmospheric pressure does influence, to a slight amount, both the latent heat of fusion and the melting point.

LIGHT.

Two views have been entertained respecting the nature of light. Newton imagined that luminous bodies emit, or shoot out, infinitely small particles in straight lines, which, by penetrating the transparent parts of the eye and falling upon the nervous tissue, produce vision. Other philosophers drew a parallel between the properties of light and those of sound, and considered that, as sound is certainly the effect of undulations, or little waves, propagated through elastic bodies in all directions, so light might be nothing more than the consequence of similar undulations transmitted with inconceivable velocity through a highly elastic medium, of excessive tenuity, filling all space, and occupying the intervals between the particles of material substances. To this medium they gave the name of *ether*. The wave hypothesis of light is at present generally adopted. It is in harmony with all the known phenomena discovered since the time of Newton, not a few of which were first deduced from the undulatory theory, and afterwards verified by experiment. Several well-known facts are in direct opposition to the theory of emission.

A ray of light emitted from a luminous body proceeds in a straight line and with extreme velocity. Certain astronomical observations afford the means of approximating to a knowledge of this velocity. The satellites of Jupiter revolve about the planet in the same manner as the moon about the earth, and the time of revolution of each satellite is exactly known from its periodical entry into or exit from the shadow of the planet. The time required by one is only 42 hours. Römer, the astronomer of Copenhagen, found that this period appeared to be longer when the earth, in its passage round the sun, moved from the planet Jupiter; and, on the contrary, he observed that the periodic time appeared to be shorter when the earth moved in the direction towards Jupiter. The difference, though very small for a single revolution of the satellite, increases, by the addition of many revolutions, during the passage of the earth from its nearest to its greatest distance from Jupiter, that is, in about half a year, till it amounts to 15 minutes and 16 seconds. Römer concluded from this, that the light of the sun, reflected from the satellite, required that time to pass through a distance equal to the diameter of the orbit of the earth; and since this space is little short of 200 millions of miles, the velocity of light cannot be less than 200,000 miles in a second of time. It will be seen hereafter that this rapidity of transmission is rivalled by that of electricity. Another astronomical phenomenon, observed and correctly explained by Bradley, the aberration of the fixed stars, leads to the same result. Physicists have, moreover, succeeded in measuring the velocity of light for terrestrial, and indeed comparatively small distances; the results of these experiments essentially correspond with those given by astronomical observations.

REFLECTION.—When a ray of light falls upon a boundary between two media, a part of it, and, in exceptional cases, the whole, is reflected into the first medium, whilst the other part penetrates into the second medium.

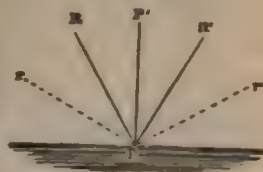
The law of regular reflection is extremely simple. If a line be drawn perpendicular to the surface upon which the ray falls, and the angle contained between the ray and the perpendicular be measured, it will be found that the ray, after reflection, takes such a course as to make with the per-

regular an equal angle on the opposite side of the latter. A ray of light, falling at the point r , will be reflected in the direction rn' , making the angle nrr' equal to the angle npp' ; and a ray from the point r' falling upon the same spot will be reflected to r in turn of the same law. Further, it is to be observed, that the incident and reflected rays are always contained in the same normal plane.

The same rule holds good if the mirror be curved, as a portion of a sphere, the surface being considered as made up of a multitude of little planes. Parallel rays are to be so when reflected from curved surfaces, becoming divergent or convergent according as the reflecting surface is convex or concave.

Bodies with rough and uneven surfaces, the smallest parts of which are turned towards each other without order, reflect the light diffused. The perception of bodies depends upon the diffused reflected light.

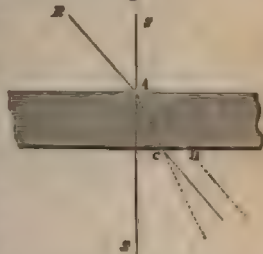
Fig. 40.



Refraction.—It has just been stated that light passes in straight lines, but this is true only so long as the medium through which it travels possesses the same density and the same material nature: when this ceases to be the case, the ray of light is bent from its course to a new one, or is said to be *refracted*.

Let a (fig. 41) be a ray of light falling upon a plate of some transparent substance with parallel sides, such as a piece of thick plate glass—in short, any transparent homogeneous material which is either non-crystalline, or crystallizes in the regular system; and let a be its point of contact with the upper surface. The ray, instead of holding a straight course and passing into the glass in the direction aa , will be bent downwards to c ; and, on leaving the glass, and issuing into the air on the other side, it will again be bent, but in the opposite direction, so as to take a parallel to the continuation of its former track, provided there be the same medium on the upper and lower side of the plate. The general law is thus expressed: When the ray passes from a rare to a denser medium, it is usually refracted *towards* a line perpendicular to the surface of the latter; and conversely, when it leaves a dense medium for a rarer medium, it is refracted *from* a line perpendicular to the surface of the denser substance; in the former case the angle of incidence is greater than that of refraction, in the latter, it is less. In both cases the direction of the refracted ray is in the plane Raa' , which is formed by the falling ray and the perpendicular aa' drawn from the spot where the ray is refracted; the angle $u a s = u a s'$, is called the angle of incidence. The angle $c a s'$ is called the angle of refraction. The difference of these two angles, that is, the angle $c a u$, is the refraction.

Fig. 41.

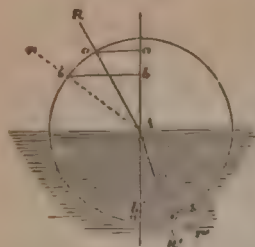


The amount of refraction, for the same medium, varies with the obliquity with which the ray strikes the surface. When perpendicular to the latter, the ray passes without change of direction at all; and in other positions, the refraction increases with the obliquity.

Let a (fig. 42) represent a ray of light falling upon the surface of a mass of plate glass at the point a . From this point let a perpendicular fall and

be continued into the new medium, and around the same point, as a centre, let a circle be drawn. According to the law just stated, the refraction must

Fig. 42



be towards the perpendicular; in the direction $a'n'$, for example. Let the lines $o-a'-a'$, at right angles to the perpendicular, be drawn, and their length compared by means of a scale of equal parts, and noted their length will, in the case supposed, be in proportion of 3 to 2. These lines are termed the *sines* of the angles of incidence and refraction respectively.

Now let another ray be taken, such as e ; it is refracted in the same manner to e' , the bending being greater from the increased obliquity of the ray; but what is very remarkable, if the sines of the two new angles of incidence and refraction be again compared, they will still be found to bear to each other

the proportion of 3 to 2. The fact is expressed by saying, that so long as the light passes from one to the other of the same two media, the *ratio of the sines of the angles of incidence and refraction is constant*. This ratio is called the *index of refraction*.

Different bodies possess different refractive powers; generally speaking, the densest substances refract most. Combustible bodies have been noticed to possess greater refractive power than their density would indicate, and from this observation Newton predicted the combustible nature of the diamond long before anything was known respecting its chemical nature.

The method adopted for describing the comparative refractive power of different bodies, is to state the ratio borne by the sine of the angle of incidence in the first medium at the boundary of the second, to the sine of the angle of refraction in this second medium; this is called the *index of refraction* of the two substances; it is greater or less than unity, according as the second medium is denser or rarer than the first. In the case of air and plate glass the index of refraction is 1.5.

When the index of refraction of any particular substance is once known, the effect of the latter upon a ray of light entering it in any position can be calculated by the law of sines. The following table exhibits the index of refraction of several substances, supposing the ray to pass into them from the air:—

| Substances. | Index of refraction. | Substances. | Index of refraction. |
|----------------------|----------------------|-------------------------------------|----------------------|
| Turbashoer* | . . 1.10 | Garnet . . . | 1.50 |
| Ice . . . | . . 1.30 | Glass with much oxide of lead . . . | 1.90 |
| Water . . . | . . 1.34 | Zircon . . . | 2.00 |
| Fluor spar . . . | . . 1.40 | Phosphorus . . . | 2.20 |
| Plate glass . . . | . . 1.50 | Diamond . . . | 2.50 |
| Rock-crystal . . . | . . 1.60 | Chromate of lead . . . | 3.00 |
| Chrysolite . . . | . . 1.69 | Cinnabar . . . | 3.20 |
| Bisulphide of carbon | 1.70 | | |

When a luminous ray enters a mass of substance differing in refractive power from the air, and whose surfaces are not parallel, it becomes permanently deflected from its course and altered in its direction. It is upon this principle that the properties of prisms and lenses depend. To take an example: Figure 43 represents a triangular prism of glass, upon the

* A siliceous deposit in the joints of the bamboo.

side of which the ray of light u may be supposed to fall. This ray will of course be refracted, on entering the glass, towards a line perpendicular to the first surface, and again, from a line perpendicular to the second surface, on emerging into the air. The result is the deflection acR , which is equal to the sum of the two deflections which the ray undergoes in passing through the prism.

A convex lens is thus enabled to converge rays of light falling upon it, and a concave lens to separate them more widely; each separate part of the surface of the lens producing its own independent effect.

DISPERSION.—The light of the sun and celestial bodies in general, as well as that of the electric spark and of all ordinary flames, is of a compound nature. If a ray of light from any of the sources mentioned be admitted into a dark room by a small hole in a shutter, or otherwise, and suffered to fall upon a glass prism, in the manner shown in fig. 44, it will



Fig. 44.



not only be refracted from its straight course, but will be decomposed into a number of colored rays, which may be received upon a white screen placed behind the prism. When solar light is employed, the colors are extremely brilliant, and spread into an oblong space of considerable length.

The prism being placed with its base upwards, as in fig. 44, the upper part of this image, or *spectrum*, will be violet and the lower red, the intermediate portion, commencing from the violet, being indigo, blue, green, yellow, and orange, all graduating imperceptibly into each other. This is the celebrated experiment of Sir Isaac Newton; from it he drew the inference that white light is composed of seven primitive colors, the rays of which are differently refrangible by the same medium, and hence capable of being thus separated. The violet rays are most refrangible, and the red rays least.*

Objects of the same refractive power do not always equally disperse or spread out the differently colored rays to the same extent; because the principal yellow or red rays, for instance, are equally refracted by two prisms of different materials, it does not follow that the blue or the violet will be similarly affected. Hence, prisms of different varieties of glass, or

* The colors of natural objects are supposed to result from the power possessed by their surfaces of absorbing some of the colored rays, while they reflect or transmit, as the case may be, the remainder of the rays. Thus an object appears red because it absorbs or causes to disappear the yellow and blue rays composing the white light by which it is illuminated. Any color which remains after the subtraction of another color from white light, is said to be *complementary* to the latter. Complementary colors, when acting simultaneously, reproduce white light. Thus, in the example already quoted, red and green are complementary colors. The fact of complementary colors giving rise to white light may be readily illustrated by mixing in appropriate quantities a rose-red solution of cobalt and green solution of nickel; the resulting liquid is nearly colorless.

other transparent substances, give, under similar circumstances, very different spectra, both as respects the length of the image, and the relative extent of the colored bands.

The appearance of the spectrum may also vary with the nature of the source of light: the investigation of these differences, however, involves the use of a more delicate apparatus. Fig. 45 shows the principle of such

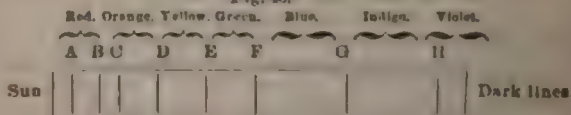
Fig. 45.



an apparatus, which is called a *spectroscope*. The light, passing through a fine slit, *s*, impinges upon a flint-glass prism, *p*, by which it is dispersed. The decomposed light emerges from the prism in several directions between *r* (red rays) and *v* (violet rays); and the spectrum thus produced is observed by the telescope, *t*, which receives only part of it at once; but the several parts may be readily examined by turning slightly either the prism or the telescope.

If the solar spectrum be examined in this manner, numerous dark lines parallel with the edge of the prism are observed. They were discovered in 1802 by Dr. Wollaston, and subsequently more minutely investigated by Fraunhofer. They are generally known as Fraunhofer's lines. These dark lines, which exist in great numbers, and of varying strength, are irregularly distributed over the whole spectrum. Some of them, in consequence of their peculiar strength and their relative position, may always be easily recognized; the more conspicuous are represented in fig. 46, and in the frontispiece. The same dark lines, though paler, and much more

Fig. 46.



difficult to recognize, are observed in the spectrum of planets lighted by the sun; for instance, in the light emanating from Venus. On the other hand, the dark lines observed in the spectra which are produced by the light emanating from fixed stars—from Sirius, for instance—differ in position from those previously mentioned.

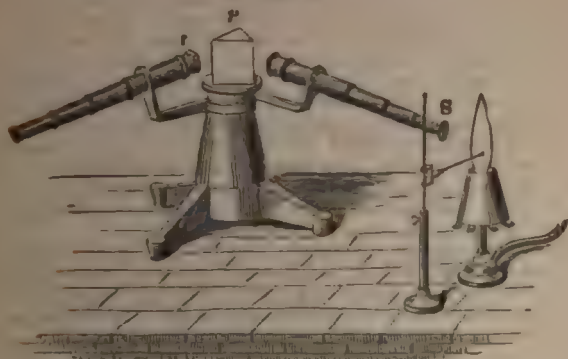
Sources of light which contain no volatile constituents—incandescence platinum wire, for example—furnish continuous spectra, exhibiting no such lines. But if volatile substances be present in the source of light, bright lines are observed in the spectrum, which are frequently characteristic of the volatile substances.

Professor Plücker, of Bonn, has investigated the spectra which are produced by the electric light when developed in very rarefied gases. He found the bright lines and the dark stripes between the lines varying considerably with different gases. When the electric light was developed in a mixture of two gases, the spectrum thus obtained exhibited simultaneously the peculiar spectra belonging to the two gases of which the mixture

consisted. When the experiment was made in gaseous compounds capable of being decomposed by the electric current, this decomposition was indicated by the spectra of the separated constituents becoming perceptible.

Many years ago, the spectra of colored flames were examined by Sir John Herschel, Fox Talbot, and W. A. Miller. Within the last few years results of the greatest importance have been obtained by Kirchhoff and Bunsen, who have investigated the spectra furnished by the incandescence of volatile substances; these researches have enriched chemistry with a new method of analysis, the analysis by spectrum observations. In order to recognize one of the metals of the alkalies or of the alkaline earths, it is generally sufficient to introduce a minute quantity of a moderately volatile compound of the metal, on the loop of a platinum wire, into the edge of the very hot, but scarcely luminous flame, of a mixture of air and coal-gas, and to examine the spectrum which is furnished by the flame containing the vapor of the metal or its compound. Fig. 47 exhibits the

Fig. 47.



apparatus which is used in performing experiments of this description. The light of the flame in which the metallic compound is evaporated passes through the fine slit in the disk, *s*, into a tube, the opposite end of which is provided with a convex lens. This lens collects the rays diverging from the slit, and throws them parallel upon the prism, *p*. The light is decomposed by the prism, and the spectrum thus obtained is observed by means of the telescope, which may be turned round the axis of the stand carrying the prism. Foreign light is excluded by an appropriate covering.

The limits of this elementary treatise do not permit us to describe the ingenious arrangements which have been contrived for sending the light from different sources through the same prism at different heights, whereby their spectra, the solar spectrum, for instance, and that of a flame, may be placed in a parallel position, the one above the other, and thus be compared.* The spectra of flames in which different substances are volatilized frequently exhibit such characteristically distinct phenomena, that they may be used with the greatest advantage for the discrimination of these substances. Thus the spectrum of a flame containing sodium (*Na*) exhibits a bright line on the yellow portion, the spectrum of potassium (*K*) a characteristic bright line at the extreme limit of the red, and another at the

* See the article "Spectral Analysis," by Prof. Roscoe, in Watts's Dictionary of Chemistry, vol. v.

opposite violet limit of the spectrum. Lithium (Li) shows a bright brilliant line in the red, and a paler line in the yellow portion; strontium (Sr) a bright line in the blue, one in the orange, and six less distinct ones in the red portion of the spectrum. The frontispiece exhibits the most remarkable of the dark lines of the solar spectrum (Fraunhofer's lines), and the position of the bright lines in the spectra of flames containing the vapors of compounds of the metals of the alkalis and alkaline earths, also of the metals thallium and indium.

The delicacy of these spectral reactions is very considerable, but unequal in the case of different metals. The presence of $\frac{1}{200,000,000}$ grain of so-

dium in the flame is still easily recognizable by the bright yellow line in the spectrum. Lithium, when introduced in the form of a volatile compound, imparts to the flame a red color; but this coloration is no longer perceptible when a volatile sodium compound is simultaneously present, the yellow coloration of the flame predominating under such circumstances. But when a mixture of one part of lithium and 1000 parts of sodium is volatilized in a flame, the spectrum of the flame exhibits, together with the bright yellow sodium line, likewise the red line characteristic of lithium. The observation of bright lines not belonging to any of the previously known bodies has led to the discovery of new elements. Thus, Bunsen and Kirchhoff, when examining the spectrum of a flame in which a mixture of alkaline salt was evaporated, observed some bright lines, which could not be attributed to any of the known elements, and were thus led to the discovery of the two new metals, cesium and rubidium. By the same method a new element, thallium, has been more recently discovered by Mr. Crookes; another, called indium, by Reich and Richter; and a third, called gallium, by Lecoq de Boisbaudran.

For the examination of the bright lines in the spectra of metals, the electric spark, passing between two points of the metal under examination, may be conveniently employed as a source of light. Small quantities of the metal are invariably volatilized; and the spectrum developed by the electric light exhibits the bright lines characteristic of the metal employed. These lines were observed by Wheatstone as early as 1835. This method of investigation is more especially applicable to the examination of the spectra of the heavy metals.

By a series of theoretical considerations, Professor Kirchhoff has arrived at the conclusion that the spectrum of an incandescent gas is reversed—i. e., that the bright lines become dark lines—if there be behind the incandescent gas a very luminous source of light, which by itself furnishes a continuous spectrum. Kirchhoff and Bunsen have fully confirmed this conclusion by experiment. Thus a volatile lithium salt produces, as just pointed out, a very distinct bright line in the red portion of the spectrum; but if bright sunlight, or the light emitted by a solid body heated to the most powerful incandescence, be allowed to fall through the flame upon the prism, the spectrum exhibits, in the place of this bright line, a black line similar in every respect to Fraunhofer's lines in the solar spectrum. In like manner the bright strontium line is reversed into a dark line. Kirchhoff and Bunsen have expressed the opinion that all the Fraunhofer lines in the solar spectrum are bright lines thus reversed. In their conception, the sun is surrounded by a luminous atmosphere, containing a certain number of volatilized substances, which would give rise in the spectrum to certain bright lines, if the light of the solar atmosphere alone could reach the prism; but the intense light of the powerfully incandescent body of the sun, which passes through the solar atmosphere, causes these bright lines to be reversed and to appear as dark lines on the ordinary

distinction, most exactly with the same number of dark lines in the spectrum, and, accordingly, he believes iron, in the state of vapor, present in the solar atmosphere. In a similar manner this physicist endeavored to establish the presence of several other elements in the atmosphere.

Absorption Spectra.—The relative quantities of the several colored rays shed by a colored medium of given thickness may be observed by passing a line of light through a prism and the colored medium; the spectrum will then be seen to be diminished in brightness in some parts, perhaps cut off altogether in others. This mode of observation is of great use in chemical analysis, as many colored substances when examined afford very characteristic spectra, the peculiarities of which often be distinguished, even though the solution of the substance examined contains a sufficient amount of colored impurities to give its color very considerably. The following method of making the observation is given by Professor Stokes.*

A small prism is to be chosen of dense flint glass, ground to an angle of about 45°, and just large enough to cover the eye comfortably. The top and bottom faces should be flat, for convenience of holding the prism between the thumb and forefinger, and laying it down on a table so as not to scratch or soil the faces. A fine line of light is obtained by making a vertical slit in a board six inches square, or a little longer in a horizontal direction, and clamping to the aperture two pieces of thin metal. One of the metal pieces should be made movable, to allow of altering the breadth of the slit. About the fiftieth of an inch is a suitable breadth for ordinary purposes. The board and the pieces should be well blackened.

Holding the board at arm's length against the sky or a luminous surface, the slit, being, we will suppose, in a vertical direction, and viewing the line of light thus formed through the prism held close to the eye, with the prism vertical, a pure spectrum is obtained at a proper azimuth of the prism. Turning the prism round its axis alters the focus, and the proper position is got by trial. The whole of the spectrum is not, indeed, in perfect

absorption might be missed. If the solution be contained in a wedge-shaped vessel instead of a test-tube, the progress of the absorption may be watched in a continuous manner by sliding the vessel before the eye. Some observers prefer using a wedge-shaped vessel in combination with the slit, the slit being perpendicular to the edge of the wedge. In this case each element of the slit forms an elementary spectrum corresponding with a thickness of the solution which increases in a continuous manner from the edge of the wedge, where it vanishes. This is the mode of observation adopted by Gladstone.*

Fig. 48 represents the effect produced in this way by a solution of chromic chloride, and fig. 49 that produced by a solution of potassium permanganate.

Fig. 48.



Fig. 49.



The right hand side of these figures corresponds with the red end of the spectrum; the letters refer to Fraunhofer's lines. The lower part of each figure shows the pure spectrum seen through the thinnest part of the wedge; and the progress of the absorption, as the thickness of the liquid increases, is seen by the gradual obliteration of the spectrum towards the upper part of the figures.

Fluorescence.—An examination into a peculiar mode of analysis of light, discovered by Sir John Herschel, in a solution of quinine sulphate, has within the last few years led to the discovery of a most remarkable fact. Professor Stokes has observed that light of certain refrangibility and color is capable of experiencing a peculiar influence in being dispersed by certain media, and of undergoing thereby an alteration of its refrangibility and color. This curious change, called fluorescence, can be produced by a great number of bodies, both liquid and solid, transparent and opaque. Frequently the change affects only the extreme limits; at other times larger portions; and in a few cases even the whole, or, at all events, the major part of the spectrum. A dilute solution of quinine sulphate, for instance, changes the violet and dark-blue light to sky-blue; by a decoction of madder in a solution of alum all rays of higher refrangibility than yellow are converted into yellow; by an alcoholic solution of the coloring matter of leaves, all the rays of the spectrum become red. In all cases in which this peculiar phenomenon presented itself in a greater or less degree, Mr. Stokes observed that it consisted in a diminution of the refrangibility. Thus, rays of so high a degree of refrangibility, that they extend far beyond the extreme limits of the spectrum visible under ordinary circumstances, may be rendered luminous, and converted into blue and even red light.

REFRACTION AND POLARIZATION.—A ray of common light made to enter certain crystals of a particular order is found to undergo a change. It becomes split or divided into two rays, one in the general law of refraction, while the other takes a new course, dependent on the position of the crystal. This, called double refraction, is beautifully illustrated in Iceland spar, or crystallized calcium carbonate. On placing a substance on a piece of white paper on which a mark or line

the object will be seen double. A ray of light be suffered to fall on a plate of glass at an angle, a portion of the ray which suffers reflection will be found to

properties which it did not before possess; if it, at the same angle, upon a second reflection will be observed that there are two parts of the latter, namely, those in which the incidence are at right angles to one another, the light is no longer reflected, but entirely transmitted. The light which has suffered this change is said

Fig. 50.



which passes through the first or polarizing plate to a certain extent, in this peculiar case, employing a series of similar plates held together, first, this effect may be greatly increased; then or twenty such plates may be used to produce convenience for the experiment. It is to be noted that the light polarized by transmission is in an opposite state to that polarized

that is, when examined by a second or analyzing plate, held before mentioned, it will be seen to be reflected when the first is transmitted, and to be dispersed when the first is reflected.

Every substance that is capable of polarizing light in this manner, water, and certain other bodies bring about the change in having a particular polarizing angle at which the effect is produced. In each transparent substance the polarizing angle is that at which the reflected and refracted rays are perpendicular to each other. Some substances polarize light, by reflection, but they do so very imperfectly. In doubly-refracting crystals are found, on examination, to be polarized in a very complete manner, and also transversely, the one being polarized when the other vanishes or is transmitted. The two rays are to be polarized in opposite directions. With a rhomb of Iceland spar of tolerably large dimensions, the two oppositely polarized rays may be widely separated and examined apart.

Doubly-refracting crystals absorb one of these rays, but not the other. In a plate of such a crystal one ray passes and becomes transmitted; the other, which is likewise polarized, but in another direction, is absorbed. The best known of these media is tourmaline. Two plates of this mineral, cut parallel to the axis of the crystal with their axes parallel, as in fig. 51, light traverses them both; but when one of them is turned round in the manner shown in fig. 52, to make the axes cross at right angles, the light is almost entirely absorbed, if the tourmalines are good. A plate of the mineral thus serves as a good test for discriminating between polarized light and unpolarized light, and does not undergo the change.

The tourmaline plate, which is always colored, frequent use of it is made in the construction of Nicol's prisms, or conjoined prisms of calcium carbonate, which, because of a peculiar cutting and combination, possess the

property of allowing only one of the oppositely polarized rays to pass. A more advantageous method of cutting and combining prisms has been given by M. Foucault. His prisms are as serviceable as, and less expensive than, those of Nichol. If two Nichol's or Foucault's prisms be placed

Fig. 51.



Fig. 52.



one behind the other, in precisely similar positions, the light polarized by the one goes through the other unaltered. But when one prism is slightly turned round in its setting, a cloudiness is produced; and by continuing to turn the prism, this increases until perfect darkness ensues. This happens, as with the tourmaline plates, when the two prisms cross one another. The phenomenon is the same with colorless as with colored light.

Circular Polarization.—Supposing that polarized light, colored, for example, by going through a plate of red glass, has passed through the first Nichol's prism, and been altogether obstructed in consequence of the position of the second prism, then, if between the two prisms a plate of rock-crystal, formed by a section at right angles to the principal axis of the crystal, be interposed, the light polarized by the first prism will, by passing through the plate of quartz, be enabled partially to pass through the second Nichol's prism. Its passage through the second prism can then again be interrupted by turning the second prism round to a certain extent. The rotation required varies with the thickness of the plate of rock-crystal, and with the color of the light employed. It increases from red in the following order—yellow, green, blue, violet.

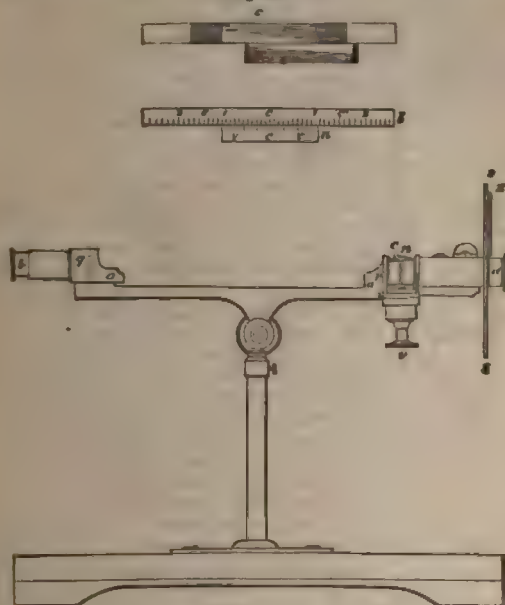
This property of rock-crystal was discovered by Arago. The kind of polarization has been called circular polarization. The direction of the rotation is with many plates towards the right hand; in other plates it is towards the left. The one class is said to possess right-handed polarization, or to be *dextrorotatory* or *dextrogyrate*; the other class, to possess left-handed polarization, or to be *levorotatory* or *levogyrate*. For a long time quartz was the only solid body known to exhibit circular polarization. Others have since been found which possess this property in a far higher degree. Thus, a plate of cinnabar acts fifteen times more powerfully than a plate of quartz of equal thickness.

Biot observed that many solutions of organic substances exhibit the property of circular polarization, though to a far less extent than rock-crystal. Thus, solutions of cane-sugar, glucose, and tartaric acid, possess right-handed polarization; whilst albumin, uncrystallizable sugar, and oil of turpentine, are left-handed. In all these solutions the amount of circular polarization increases with the concentration of the liquid, and the thickness of the column through which the light passes. Hence, circular polarization is an important auxiliary in chemical analysis. In order to determine the amount of polarization which any liquid exhibits, it is put into a glass tube not less than from ten to twelve inches long, which is closed with glass plates. This is then placed between the two Nichol's prisms, which have previously been so arranged with regard to each other that no light could pass through. An apparatus of this description, the

polarimeter, is used for determining the concentration of solutions of sugar.

A form of this instrument is shown in fig. 53. The two Nicol's prisms are inclosed in the corresponding fastenings *a* and *b*. Between the prisms there is a space to receive the tube, which is filled with the solution of sugar. If the prisms are crossed in the way above mentioned before

Fig. 53.



the tube is put in its place, that is, if they are placed so that no light passes through them, then, by the action of the solution of sugar, the light is enabled to pass, and the Nicol's prism, *a*, must be turned through a certain angle before the light is again perfectly stopped. The magnitude of this angle is observed on the circular disk *s s*, which is divided into degrees, and upon which, by the turning of the prism, an index *z* is moved along the division. When the tube is exactly ten inches long, and closed at both ends by flat glass plates, and when it is filled with solution containing 10 per cent. by weight of cane-sugar, and free from any other substance possessing an action on light, the angle of rotation for the middle yellow ray is 19.6° . Now, the magnitude of this angle is directly proportional to the length of the column of liquid, and also to the quantity of sugar in solution. If, therefore, a solution containing *z* per cent. by weight of sugar in a tube *l* inches long, produce a rotation equal to *a* degrees, the percentage of sugar will be given by the equation—

$$\frac{a}{19.6} = \frac{l}{10} \cdot \frac{z}{10},$$

hence,

$$z = \frac{100 a}{19.6 l}.$$

This process is not sufficient when the solution contains cane-sugar and uncrystallizable sugar; for the latter rotates the ray to the left; in that case only the difference of the two actions is obtained. But if the whole quantity of sugar be changed into uncrystallizable sugar, and the experiment be repeated, then from the results of the two observations the quantity of both kinds of sugar can easily be calculated.

It is difficult to find exactly that position of the Nicol's prisms in which the greatest darkness prevails. To make the measurements more exact and easy, Soleil has made some additions to the apparatus. At *q*, before the prism *b*, a plate of rock-crystal cut at right angles to the axis is placed. It is divided in the centre of the field of vision, half consisting of quartz rotating to the right hand, and half of the variety which rotates to the left; it is 0.148 inch (3.75 millimetres) thick, this thickness being found by experiment to produce the greatest difference in the color of the two halves, when one prism is slightly rotated. The solution of sugar has precisely the same action on the rotation, since it increases the action of the half which has a right-handed rotation, and lessens the action of the half which rotates to the left. Hence the two halves will assume a different color when the smallest quantity of sugar is present in the liquid. By slightly turning the Nicol's prism *a*, this difference can be again removed. Soleil has introduced another more delicate means of effecting this, at the part *l*, which he calls the compensator. The most important parts of this are separately represented in fig. 53. It consists of two exactly equal right-angled prisms, of left-handed quartz, whose surfaces, *c* and *c'*, are cut perpendicular to the optic axis. These prisms can, by means of the screw *e* and a rack and pinion, be made to slide on one another, so that, when taken together, they form a plate of varying thickness, bounded by parallel surfaces. One of the frames has a scale *l*, the other a vernier *n*. When this points to zero of the scale, the optical action of the two prisms is exactly compensated by a right-handed plate of rock-crystal, so that an effect is obtained as regards circular polarization, as if the whole system were not present. As soon, however, as the screw is moved, and thus the thickness of the plate formed by the two prisms is changed (we will suppose it increased), then a left-handed action ensues, which must be properly regulated, until it compensates the opposite action of a solution of sugar. Thus a convenient method is obtained of rendering the color of the double plate uniform, when it has ceased to be so by the action of the sugar.

Faraday made the remarkable discovery that, if a very strong electric current be passed round a substance which possesses the property of circular polarization, the amount of rotation is altered to a considerable degree.

HEATING AND CHEMICAL RAYS OF THE SOLAR SPECTRUM.—The luminous rays of the sun are accompanied, as already mentioned, by others which possess heating powers. If the temperature of the different colored spaces in the spectrum be tried with a delicate thermometer, it will be found to increase from the violet to the red extremity, and when the prism is of some particular kinds of glass, the greatest effect will be manifested a little beyond the visible red rays. The position of the greatest heating effect in the spectrum materially depends on the absorptive nature of the glass. Transparent though this medium is to the rays of light, it nevertheless absorbs a considerable quantity of the heat rays. Transparent rock-salt is almost without absorptive action on the thermal rays. In the spectrum obtained by passing the solar rays through prisms of rock-salt, the greatest thermal effect is found at a position far beyond the last visible

red rays. It is inferred from this that the chief mass of the heating rays of the sun are among the least refrangible components of the solar beam.

Again, it has long been known that chemical changes both of combination and of decomposition, but more particularly the latter, can be effected by the action of light. Chlorine and hydrogen combine at common temperatures only under the influence of light; and parallel cases occur in great numbers in organic chemistry. The blackening and decomposition of silver salts are familiar instances of the chemical powers of the same agent. Now, it is not always the luminous part of the ray which effects these changes; they are chiefly produced by certain invisible rays, which accompany the others, and are found most abundantly beyond the violet part of the spectrum. It is there that certain chemical effects are most marked, although the intensity of the light is exceedingly feeble. These chemically acting rays are sometimes called *actinic rays* (*actis*, a ray), and the chemical action of sunlight is called *actinism*; but these terms are not very well chosen. The chemical rays are thus directly opposed to the heating rays in the common spectrum in their degree of refrangibility, since they exceed all the others in this respect. The luminous rays, too, under peculiar conditions, exert decomposing powers upon silver salts. The result of the action of any ray depends, moreover, greatly on the physical state of the surface on which it falls, and on the chemical constitution of the body: indeed, for every kind of ray a substance may be found which under particular circumstances will be affected by it; and thus it appears that the chemical functions are by no means confined to any set of rays to the exclusion of the rest.

Upon the chemical changes produced by light is based the art of *photography*. In the year 1802 Mr. Thomas Wedgwood proposed a method of copying paintings on glass, by placing behind them white paper or leather saturated with a solution of silver nitrate, which became decomposed and blackened by the transmitted light in proportion to the intensity of the latter; and Davy, in repeating these experiments, found that he could thus obtain tolerably accurate representations of objects of a texture partly opaque and partly transparent, such as leaves and the wings of insects, and even copy with a certain degree of success the images of small objects obtained by the solar microscope. These pictures, however, required to be kept in the dark, and could only be examined by candle-light, otherwise they became obliterated by the blackening of the whole surface, from which the salt of silver could not be removed. These attempts at light-printing attracted but little notice till the year 1839, when Mr. Fox Talbot published his plan of "photogenic drawing." This consisted in exposing in the camera a paper soaked in a weak solution of common salt, and afterwards washed over with a strong solution of nitrate of silver; the image thus obtained was a *negative* one, the lights being dark and the shadows light, and the pictures were fixed by immersion in a solution of common salt.

Many improvements have been made in this process. In 1841 Fox Talbot patented the beautiful process known as the "Talbotype or Calotype process," in which the paper is coated with silver iodide by dipping it first in silver nitrate, then in potassium iodide.

Paper thus prepared is not sensitive *per se* to the action of light, but may be rendered so by washing it over with a mixture of silver nitrate and gallic or acetic acid. If it be exposed in the camera for two or three minutes, it does not receive a visible image (unless the light has been very strong), but still the compound has undergone a certain change by the influence of the light; for on subsequently washing it over with the mixture of silver nitrate and acetic or gallic acid, and gently warming it, a negative image comes out on it with great distinctness. This image is

fixed by washing the paper with sodium hyposulphite, which removes the whole of the silver iodide not acted upon by the light, and thus protects the picture from further change by exposure to light. The negative picture thus obtained is rendered transparent by placing it between two sheets of blotting-paper saturated with white wax, and passing a moderately heated smoothing-iron over the whole. It may then be used for printing *positive pictures* by laying it on a sheet of paper prepared with chloride or iodide of silver and exposing it to the sun.

A most important step in the progress of photography is the substitution of a transparent film of iodized collodion or albumin spread upon glass, for the iodized paper used in Talbot's process, to receive the negative image in the camera. The process is thus rendered so much more certain and rapid, and the positive pictures obtained by transferring the negative to paper prepared with chloride or iodide of silver are found to be so much sharper in outline, than when the transference occurs through paper, as in the talbotype process, that this method is now universally employed. In this process, as in that of the Calotype, the image produced in the camera is a latent one, and requires development with substances such as pyrogallie acid, or ferrous sulphate, which, having a tendency to absorb oxygen, induce, in presence of silver nitrate, the reduction of the chloride or iodide to the metallic state. For a description of the best apparatus and latest processes used in the collodion method, the reader may consult Hardwich's "Manual of Photographie Chemistry."

Sir John Herschel has shown that a great number of other substances can be employed in these photographic processes by taking advantage of the deoxidizing effects of certain portions of the solar rays. Paper washed with a solution of ferric salt becomes capable of receiving impressions of this kind, which may afterwards be made evident by potassium ferriyanide, or gold chloride. Vegetable colors are also acted upon in a very curious and apparently definite manner by the different parts of the spectrum.

The *daguerreotype*, the announcement of which was first made in the summer of 1839, by M. Daguerre, who had been occupied with this subject from 1826, if not earlier, is another remarkable instance of the decomposing effects of the solar rays. A clean and highly polished plate of silvered copper is exposed for a certain time to the vapor of iodine, and then transported to the camera obscura. In the most improved state of the process, a very short time suffices for effecting the necessary change in the film of silver iodide. The picture, however, becomes visible only by exposing it to the vapor of mercury, which attaches itself, in the form of exceedingly minute globules, to those parts which have been most acted upon, that is to say, to the lights, the shadows being formed by the dark polish of the metallic plate. Lastly, the plate is washed with sodium hyposulphite, to remove the undecomposed silver iodide and render it permanent.

Since Daguerre's time this process has undergone considerable improvements; amongst these, we may mention the exposure of the plate to the vapor of bromine, by which the sensitiveness of the film is greatly increased, and the reduction of metallic gold upon the surface of the film during the process of fixing, by which the lights and shades of the picture are rendered more effective.

Etching and lithographic processes, by combined chemical and photographic agency, promise to be of considerable utility. The earliest is that of Niépce: he applied a bituminous coating to a metal plate, upon which an engraving was superimposed. The light, being thus partially interrupted, acted unequally upon the varnish; a liquid hydro-carbon, *petroleum*, used as a solvent, removed the bitumen wherever the light had not

an engraving acid could now bite the unprotected metal, which is eventually be printed from in the usual way. Very successful results have also been obtained by M. Fizeau, who submits the daguerreotype to the action of a mixture of dilute nitric acid, common salt, and potassium iodide, when the silver only is attacked, the mercurialized portion of the plate resisting the acid; an etching is thus obtained following minutely the lights and shadows of the picture. To deepen this etching, the silver side formed is removed by ammonia, the plate is boiled in caustic soda and again treated with acid, and so on till the etching is of sufficient depth. Sometimes electro-gilding is resorted to, and an engraving is used to get still more powerful impressions.

Among recent results are those obtained by Mr. Talbot on steel plates: he uses a mixture of potassium bichromate and gelatin, which hardens by exposure to the light; the parts not affected are removed by washing. Chromic tetrachloride is used as an etching liquid; it has the advantage of acting with greater regularity than nitric acid.

The bitumen process of M. Niépce has been applied to lithographic stone; positives obtained from negative talbotypes have been printed off by a modification of the ordinary lithographic process. M. Niépce finds that nitric acid dissolves the altered bitumen, while naphtha, or benzol, attacks by dissolving the bitumen in its normal condition.

MAGNETISM.

A PARTICULAR species of iron ore has long been remarkable for its property of attracting small pieces of iron, and causing them to adhere to its surface ; it is called loadstone or magnetic iron ore.

If a piece of this loadstone be carefully examined, it will be found that the attractive force for particles of iron is greatest at certain particular points of its surface, while elsewhere it is much diminished, or even altogether absent. These attractive points are denominated poles, and the loadstone itself is said to be endowed with magnetic polarity.

If one of the pole-surfaces of a natural loadstone be rubbed in a particular manner over a bar of steel, its characteristic properties will be communicated to the bar, which will then be found to attract iron filings like the loadstone itself. Further, the attractive force will appear to be greatest at two points situated very near the extremities of the bar, and least of all towards the middle. The bar of steel so treated is said to be magnetized, or to constitute an artificial magnet.

When a magnetized bar or natural magnet is suspended at its centre in any convenient manner, so as to be free to move in a horizontal plane, it is always found to assume a particular direction with regard to the earth, one end pointing nearly north, and the other nearly south. This direction varies with the geographical position of the place, and is different also at the same place at different times. In London, at the present time, the needle points $19^{\circ} 32'$ west of the astronomical north. If the bar be moved from this position, it will tend to reassume it, and, after a few oscillations, settle at rest as before. The pole which points towards the astronomical north is usually distinguished as the north pole of the bar, and that which points southward as the south pole.

A magnet, either natural or artificial, of symmetrical form, suspended in the presence of a second magnet, serves to exhibit certain phenomena of attraction and repulsion which deserve particular attention. When a north pole is presented to a south pole, or a south pole to a north, attraction ensues between them ; the ends of the bars approach each other, and, if permitted, adhere with considerable force ; when, on the other hand, a north pole is brought near a second north pole, or a south pole near another south pole, mutual repulsion is observed, and the ends of the bars recede from each other as far as possible. *Poles of an opposite name attract, and poles of a similar name repel each other.* Thus, a small bar or needle of steel, properly magnetized and suspended, and having its poles marked, becomes an instrument fitted not only to discover the existence of magnetic power in other bodies, but to estimate the kind of polarity affected by their different parts.

A piece of soft iron brought into the neighborhood of a magnet acquires itself magnetic properties : the intensity of the power thus conferred depends upon that of the magnet, and upon the space which divides the two, becoming greater as that space decreases, and greatest of all in actual contact. The iron, under these circumstances, is said to be magnetized by *induction* or *influence*, and the effect, which reaches its maximum in an instant, is at once destroyed by removing the magnet.

When steel is substituted for iron in this experiment, the inductive action is hardly perceptible at first, and becomes manifest only after the

of a certain time: in this condition, when the steel bar is removed from the magnet, it retains a portion of the induced polarity. It becomes, in fact, a permanent magnet, similar to the first, and retains its peculiar properties for an indefinite time. This resistance which steel always offers in greater or less degree both to the development of magnetism and to its subsequent destruction, is called *specific magnetic power*.

The rule which regulates the induction of magnetic polarity in all cases is exceedingly simple, and most important to be remembered. The pole produced is always of the opposite name to that which produced it, a north pole inducing south polarity, and a south pole north polarity. The north pole of the magnet figured in the sketch induces south polarity in all the nearer extremities of the pieces of iron or steel which surround it, and a state similar to its own in all the more remote extremities. The iron thus magnetized is capable of exerting a similar inductive action on a second piece, and that upon a third, and so to a great number, the intensity of the force diminishing as the distance from the permanent magnet increases. It is in this way that a magnet is enabled to hold up a number of small pieces of iron, or a bunch of filings, each separate piece becoming for the time a magnet by induction.

Magnetic polarity, similar in degree to that which iron presents, has been found only in some of the compounds of iron, in nickel, and in cobalt.

Magnetic attractions and repulsions are not in the slightest degree interfered with by the interposition of substances destitute of magnetic properties. Thick plates of glass, shellac, metals, wood, or of any substances except those above mentioned, may be placed between a magnet and a suspended needle, or a piece of iron under its influence, the distance being preserved, without the least perceptible alteration in its attractive power, or force of induction.

One kind of polarity cannot be exhibited without the other. In other words, a magnetic pole cannot be isolated. If a magnetized bar of steel be broken at its neutral point, or in the middle, each of the broken ends requires an opposite pole, so that both portions of the bar become perfect magnets; and, if the division be carried still further, if the bar be broken into a hundred pieces, each fragment will be a complete magnet, having its own north and south poles.

This experiment serves to show very clearly that the apparent polarity of the bar is the consequence of the polarity of each individual particle, the poles of the bar being merely points through which the resultants of all these forces pass: the largest magnet is made up of an immense number of little magnets regularly arranged side by side, all having their north poles looking one way, and their south poles the other. The middle portions of such a system cannot possibly exhibit attractive or repulsive effects on an external body, because each pole is in close juxtaposition with one of an opposite name and of equal power. Hence their forces will be exerted in opposite directions, and neutralize each other's influence.

Fig. 54.



Such will not be the case at the extremities of the bar; there uncompensated polarity will be found, capable of exerting its specific power.

Fig. 66.



This idea of regular polarization of particles of matter in virtue of a pair of opposite and equal forces, is not confined to magnetic phenomena; it is the leading principle in electrical science, and is constantly reproduced in some form or other in every discussion involving the consideration of molecular forces.

Artificial steel magnets are made in a great variety of forms; such as small light needles, mounted with an agate cap for suspension upon a fine point, straight bars of various kinds; bars curved into the shape of a horse-shoe, etc. All these have regular polarity communicated to them by certain processes of rubbing or touching with another magnet, which require care, but are not otherwise difficult of execution. When great power is wished for, a number of bars may be screwed together, with their similar ends in contact, and in this way it is easy to construct permanent steel magnets capable of sustaining great weights. To prevent the gradual destruction of magnetic force, which would otherwise occur, it is usual to arm each pole with a piece of soft iron or keeper, which, becoming magnetized by induction, serves to sustain the polarity of the bar, and in some cases even increases its energy.

Magnetism is not peculiar to these substances which have more especially been called magnetic, such as iron, nickel, cobalt, but it is the property of all metals, though to a much smaller degree. Very powerful magnets are required to show this remarkable fact. Large horse-shoe magnets, made by the action of the electric current, are best adapted for the purpose. The magnetic action on different substances which are capable of being easily moved, differs not only according to the size, but also according to the nature of the substance. In consequence of this, Faraday divides all bodies into two classes. He calls the one magnetic, or, better, *paramagnetic*, and the other *diamagnetic*.

The matter of which a paramagnetic (magnetic) body consists is attracted by both poles of the horse-shoe magnet; on the contrary, the matter of a diamagnetic body is repelled. When a small iron bar is hung by untwisted silk between the poles of the magnet, so that its long diameter can easily move in a horizontal plane, it arranges itself axially, that is, parallel to the straight line which joins the poles, or to the magnetic axis of the poles, assuming at the end which is nearest the north pole, a south pole, and at the end nearest the south pole, a north pole. Whenever the little bar is removed from this position, it returns, after a few oscillations, to its previous position. The whole class of paramagnetic bodies behave in a precisely similar way under similar circumstances, but in the intensity of the effects great differences occur.

Diamagnetic bodies, on the contrary, have their long diameters placed equatorially, that is, at right angles to the magnetic axis. They behave as if at the end opposite to each pole of the magnet the same kind of polarity existed.

In the first class of substances, besides iron, which is the best representative of the class, we have nickel, cobalt, manganese, chromium, cerium,

osmium, palladium, platinum, osmium, aluminium, oxygen, and also most of the compounds of these bodies, most of them, even when in solution. According to Faraday, the following substances are also feebly paramagnetic (magnetic).—paper, sealing-wax, Indian-ink, porcelain, asbestos, turpentine, minium, cinnabar, binoxide of lead, sulphate of zinc, tourmaline, paper, and charcoal.

In the second class are placed bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, arsenic, uranium, rhodium, iridium, tungsten, phosphorus, iodine, sulphur, chlorine, hydrogen, and many of their compounds. Also, glass free from iron, water, alcohol, ether, nitric acid, hydrochloric acid, resin, wax, olive oil, oil of turpentine, acetone, sugar, starch, gum, and wood. These are diamagnetic.

When diamagnetic and paramagnetic bodies are combined, their peculiar properties are more or less neutralized. In most of these compounds, especially in consequence of the presence of a very small quantity of iron, the peculiar magnetic power remains more or less in excess. Thus green bottle-glass, and many varieties of crown glass are magnetic in consequence of the iron they contain.

In order to examine the magnetic properties of liquids, they are placed in very thin glass tubes, the ends of which are then closed by melting; they are then hung horizontally between the poles of the magnet. Under the influence of poles sufficiently powerful, they begin to swing, and according as the fluid contents are paramagnetic (magnetic) or diamagnetic, they assume an axial or equatorial position.

Faraday has tried the magnetic condition of gases in different ways. One method consisted in making soap-bubbles with the gas which he wished to investigate, and bringing these near the poles. Soap and water alone are feebly diamagnetic. A bubble filled with oxygen was strongly attracted by the magnet. All other gases in the air are diamagnetic, that is, they are repelled. But, as Faraday has shown, in a different way, this partly arises from the paramagnetic (magnetic) property of the air. Thus he found that nitrogen, when this differential action was eliminated, was perfectly indifferent, whether it was condensed or rarefied, whether cooled or heated. When the temperature is raised, the diamagnetic property of gases in the air is increased. Hence, the flame of a candle or of hydrogen is strongly repelled by the magnet. Even warm air is diamagnetic in cold air.

For some time it had been believed that crystallized bodies exhibited a special and peculiar behavior when placed between the poles of a magnet. It appeared as though the magnetic directing power of the crystal had some peculiar relation to the position of its optic axis; so that, independently of the magnetic property of the substance of the crystal, if the crystal were positively optical, it possessed the power of placing its optic axis parallel with the line which joined the poles of the magnet, while optically negative crystals tried to arrange their axis at right angles to this line. This supposition is disproved by the excellent investigation of Tyndall and Knoblauch, who showed that exceptions to the above law are furnished by all classes of crystals, and proved that the action, instead of being independent of the magnetic nature of the mass, was completely reversed where, in isomorphous crystals, a magnetic constituent was substituted for a diamagnetic one. Rejecting the various new forces assumed, Tyndall and Knoblauch referred the observed phenomena to the modification of the magnetic force by structure, and they imitated the effects exactly by means of substances whose structure had been modified by compression. In a later investigation Tyndall demonstrated the fundamental principle on which these phenomena depend, showing that the *entire mass* of a magnetic body is most strongly attracted when the attracting force acts parallel

to the line of compression; and that a diamagnetic substance is most strongly repelled when the repulsion acts along the same line. Hence, when such a body is freely suspended in the magnetic field, the line of compression must set axially or equatorially, according as the mass is magnetic or diamagnetic. Faraday was the first to establish a differential action of this kind in the case of bismuth; Tyndall extended it to several magnetic and diamagnetic crystals, and showed that it was not confined to them, but was a general property of matter. It was also proved that, for a fixed distance, the attraction of a magnetic sphere, and the repulsion of a diamagnetic sphere, followed precisely the same law, both being exactly proportioned to the square of the exciting current.

The phenomena of diamagnetism naturally suggest the inquiry, whether the repulsion exerted by a magnetic pole on diamagnetic bodies is a force distinct from that of magnetism as exerted upon iron and other bodies of the magnetic class; or whether, on the other hand, the magnetic and diamagnetic conditions of matter are merely relative, so that all bodies are magnetic in different degrees, and the apparent repulsion of a diamagnetic body, such as bismuth, is merely the result of its being attracted by the magnet less than the particles of the surrounding medium, just as a balloon recedes from the earth because its weight is less than that of an equal bulk of the surrounding air. It is easy to show that the same body may appear magnetic or diamagnetic, according to the medium in which it is placed. Ferrous sulphate is a magnetic substance, and water is diamagnetic; hence it is possible, by varying the strength of an aqueous solution of this salt, to make it either magnetic, indifferent, or diamagnetic, when suspended in air. Again, a tube containing a solution of ferrous sulphate suspended horizontally within a jar also filled with a solution of the same salt, and placed between the poles of two powerful electro-magnets, will place itself axially or equatorially, according as the solution contained in it is stronger or weaker than that in the jar. In the same manner, then, we may conceive that bismuth places itself equatorially between two magnetic poles, because it is less magnetic than the surrounding air. But the diamagnetism of bismuth and other bodies of the same class shows itself in a vacuum as well as in air; hence, if diamagnetism is not to be regarded as a distinct force, we must suppose that the *ether* is also magnetic, and occupies in the magnetic scale the place intermediate between magnetic and diamagnetic bodies.

That a body suspended in a medium of greater magnetic susceptibility than itself will recede from a magnetic pole in its neighborhood, in consequence of the greater force with which the particles of the medium are impelled towards the magnet, is so obvious a consequence of mechanical laws, that we can scarcely avoid attributing the movements of diamagnetic bodies to the cause just mentioned; at least, when the body is suspended in air or other magnetic gas. There is, however, some difficulty in reconciling the above-described phenomena of compressed and crystallized bodies with this view; and, moreover, Tyndall has shown, by a method which we cannot here describe,* that diamagnetic bodies possess opposite poles, analogous to those of magnetic bodies, each of these poles being attracted by one pole of a magnet, and repelled by the other. This polarity shows decidedly that the properties of diamagnetic bodies cannot be wholly due to the differential action above mentioned; for if they were, every part of a diamagnetic body would be repelled by either pole of a magnet. Diamagnetism must therefore, for the present at least, be regarded as a force distinct from magnetism.

* Phil. Trans., 1856 and 1858; see also Watts's Dictionary of Chemistry, vol. III. p. 576.

ELECTRICITY.

When glass, amber, or sealing-wax is rubbed with a dry cloth, it acquires the power of attracting light bodies, as feathers, dust, or bits of paper; this is the result of a new and peculiar condition of the body rubbed, called electrical excitation.

If a light downy feather be suspended by a thread of white silk, and a dry glass tube, excited by rubbing, be presented to it, the feather will be strongly attracted to the tube, adhere to its surface for a few seconds, and then fall off. If the tube be now excited anew, and presented to the feather, the latter will be strongly repelled.

The same experiment may be repeated with shellac or resin; the feather in its ordinary state will be drawn towards the excited body, and, after touching, again driven from it with a certain degree of force.

Now, let the feather be brought into contact with the excited glass, so as to be repelled by that substance, and let a piece of excited sealing-wax be presented to it; a degree of attraction will be observed far exceeding that exhibited when the feather is in its ordinary state. Or, again, let the feather be made repulsive for sealing-wax, and then the excited glass be presented: strong attraction will ensue.

The reader will at once see the perfect parallelism between the effects described and some of the phenomena of magnetism, the electrical excitement having a twofold nature, like the opposite polarities of the magnet. A body to which one kind of excitement has been communicated is attracted by another body in the opposite state, and repelled by one in the same state: the excited glass and resin being to each other as the north and south poles of a pair of magnetized bars.

To distinguish these two different forms of excitement, terms are employed which, although originating in some measure in theoretical views of the nature of the electrical disturbance, may be understood by the student as purely arbitrary and distinctive: it is customary to call the electricity manifested by glass rubbed with silk *positive* or *vitreous*, and that developed in the case of shellac, and bodies of the same class, rubbed with flannel, *negative* or *resinous*. The kind of electricity depends in some measure upon the nature of the surface and the quality of the rubber; smooth and perfectly clean glass, rubbed with silk, becomes positive, but when ground or roughened by sand or emery, it acquires under the same circumstances, a negative charge. Glass dried over a gas flame and rubbed with wool is generally also negative; when dried over a fire of wood-charcoal it remains positive.

The repulsion shown by bodies in the same electrical state is taken advantage of to construct instruments for indicating electrical excitement and pointing out its kind. Two balls of elder pith, hung by threads or very fine metal wires, serve this purpose in many cases: they open out when excited, in virtue of their mutual repulsion, and show by the degrees of divergence the extent to which the excitement has been carried. A pair of gold leaves suspended to a metal rod having a brass plate on its upper end constitute a much more delicate arrangement, and one of great value in all electrical investigations. The rod should be covered with a thick coating of shellac, and it must be fastened by means of a cork, air-tight, into a glass flask. The flask must have been perfectly dried previously

by warming it. These instruments are called *electroscopes* or *electrometers*: when excited by the communication of a known kind of electricity, they show, by an increased or diminished divergence, the state of an electrified body brought into their neighborhood (fig. 57).

Fig. 56.



Fig. 57.



One kind of electricity can no more be developed without the other than one kind of magnetism: the rubber and the body rubbed always assume opposite states, and the positive condition on the surface of a mass of matter is invariably accompanied by a negative state in all surrounding bodies.

The induction of magnetism in soft iron has its exact counterpart in electricity; a body already electrified disturbs or polarizes the particles of all surrounding substances in the same manner and according to the same law, inducing a state opposite to its own in the nearer portions, and a similar state in the more remote parts. A series of globes suspended by silk threads, in the manner represented in fig. 58, will each become electric by

Fig. 58.



induction when a charged body is brought near the end of the series, like so many pieces of iron in the vicinity of a magnet, the positive half of each globe looking in one and the same direction, and the negative half in the opposite one. The positive and negative signs are intended to represent the opposite states.

The intensity of the induced electrical disturbance diminishes with the distance from the charged body; if this be removed or discharged, all the effects cease at once.

So far, the greatest resemblance may be traced between these two sets of phenomena; but here it ceases in great measure to cease. The magnetic polarity of a piece of steel can awaken polarity in a second piece in contact with it by the act of induction, and in so doing loses nothing whatever of its power; this is an effect completely different from the apparent trans-

the discharge of electricity constantly witnessed, which in the air and vapors often gives rise to the appearance of a bright spark of fire. The ordinary magnetic effects comprise two groups of phenomena only, namely, of attraction and repulsion, and those of induction. But electricity, in addition to phenomena very closely resembling these, we have the effects of *discharge*, to which there is nothing analogous in magnetism, and which takes place in an instant when any electrified body is in communication with the earth by any one of the class of substances called conductors of electricity, all signs of electrical disturbance then ceasing.

Good conductors of electricity, which thus permit discharge to take place through their mass, are contrasted with another class of substances called non-conductors or insulators. The difference, however, is only one of degree, not of kind; the very best conductors offer a certain resistance to the electrical discharge, and the most perfect insulators permit it to a certain extent. The metals are by far the best conductors; glass, silk, resin, and dry gas, or vapor of any sort, the very worst; and between these there are bodies of all degrees of conducting power.

In good conductors of sufficient size electrical discharges take place easily and without disturbance. But if the charge be very intense, and the conductor very small, or imperfect from its nature, it is often destroyed with violence.

When a break is made in a conductor employed in effecting the discharge of a highly excited body, disruptive or spark-discharge takes place across the intervening air, provided the ends of the conductor be not too distant. The electrical spark itself presents many points of interest in the modifications to which it is liable.

The time of transit of the electrical wave through a chain of good conducting bodies of great length is so minute as to be altogether inappreciable by ordinary means of observation. Professor Wheatstone's very ingenious experiments on the subject give, in the instance of motion through a copper wire, a velocity surpassing that of light.

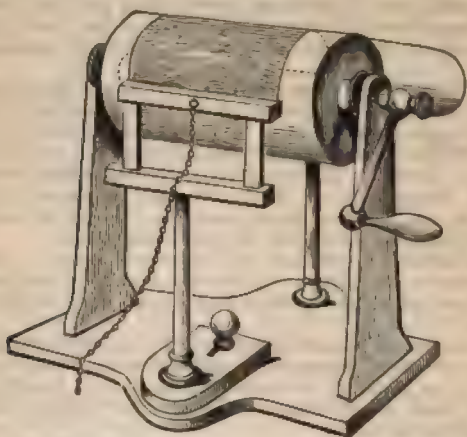
Electrical excitation is manifested only upon the surfaces of conductors, or those portions directed towards other objects capable of assuming the opposite state. An insulated ball charged with positive electricity, and placed in the centre of the room, is maintained in that state by the induction action of the walls of the apartment, which immediately become negatively electrified; in the interior of the ball there is absolutely no electricity to be found, although it may be constructed of open metal gauze, with meshes half an inch wide. Even on the surface the distribution of electrical force is not always the same; it depends upon the figure of the body itself and its position with regard to surrounding objects. The polarity is always highest in the projecting extremities of the same conducting mass, and greatest of all when these are attenuated to points; in which case the inequality becomes so great that discharge takes place to the air, and the excited condition cannot be maintained.

By the aid of these principles, the construction and use of the common electrical machine, and other pieces of apparatus of great utility, will become intelligible.

A glass cylinder (fig. 59) is mounted with its axis in a horizontal position, and provided with a handle or winch by which it may be turned. A leather cushion is made to press by a spring against one side of the cylinder, while a large metal conducting body, armed with a number of points next the glass, occupies the other: both cushion and conductor are insulated by glass supports, and to the upper edge of the former a piece of silk is attached long enough to reach half round the cylinder. Upon the

cushion is spread a quantity of soft amalgam of tin, zinc, and mercury,* mixed up with a little grease: this substance is found by experience to excite glass most powerfully. The cylinder, as it turns, becomes charged by friction against the rubber, and as quickly discharged by the row of

Fig. 79.



points attached to the great conductor; and as the latter is also completely insulated, its surface speedily acquires a charge of positive electricity, which may be communicated by contact to other insulated bodies. The maximum effect is produced when the rubber is connected by a chain or wire with the earth. If negative electricity be wanted, the rubber must be insulated and the conductor discharged.

Another form of the electrical machine consists of a circular plate of glass (fig. 80) moving upon an axis, and provided with two pairs of cushions or rubbers, attached to the upper and lower parts of the wooden frame, covered with amalgam, between which the plate moves with considerable friction. An insulated conductor, armed as before with points, discharges the plate as it turns, the rubber being at the same time connected with the ground by the wood-work of the machine, or by a strip of metal. This form of the apparatus is preferred in all cases where considerable power is wanted.

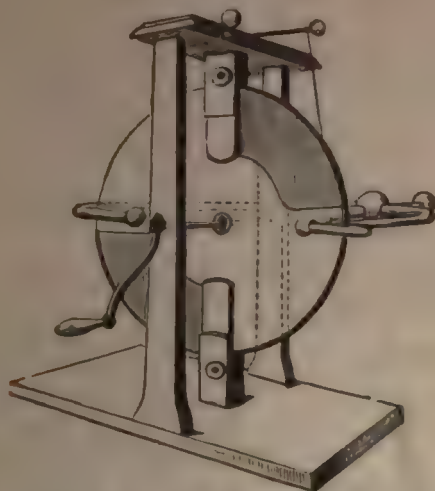
In the management of electrical apparatus, great care must be taken to prevent deposition of moisture from the air upon the surface of the glass supports, which should always be varnished with fine lac dissolved in alcohol; the slightest film of water is sufficient to destroy the power of insulation. The rubbers also must be carefully dried, and, like the plate, cleansed from adhering dust before use, and the amalgam renewed if needful: in damp weather much trouble is often experienced in bringing the machine into powerful action.

When the conductor of the machine is charged with electricity, it acts indirectly on, and accumulates the contrary electricity to its own, at the

* 1 part tin, 1 zinc, and 8 mercury. An amalgam of permanent softness and great efficacy is obtained by mixing 65 parts mercury, 24 tin, and 11 zinc. It is better applied to silk than to leather.

surface of all the surrounding conductors. It produces the greatest effect on the conductor that is nearest to it and is in the best connection with the ground, whereby the electricity of the same kind as that of the machine may pass to the earth. As the inducing electricity attracts the induced

Fig. 60.



electricity of an opposite kind, so, on the other hand, is the former attracted by the latter. Hence, the electricity which the conductor receives from the machine must especially accumulate at that spot to which another good conductor of electricity is opposed. If a metal disk is in connection with the conductor of a machine, and if another similar disk, in good connection with the earth, is placed opposite to it, we have an arrangement by which tolerably large and good conducting surfaces can be brought close to one another: thus the positive condition of the first disk, as well as the negative condition of the other, must be increased to a very considerable degree: the limit is in this case, however, soon reached, because the intervening air easily permits spark-discharge to take place through its substance. With a solid insulating body, as glass or lac, this happens with much greater difficulty, even when the plate of insulating matter is very thin. It is on this principle that instruments for the accumulation of electricity depend, among which the Leyden jar is the most important.

A thin glass jar is coated on both sides with tinfoil, care being taken to leave several inches of the upper part uncovered (fig. 61): a wire, terminating in a metallic knob, communicates with the internal coating. When the outside of the jar is connected with the earth, and the knob put in contact with the conductor of the machine, the inner and outer surfaces of the glass become respectively *positive* and *negative*, until a very great degree of intensity has been attained. On completing the connection be-

Fig. 61.



tween the two coatings by a metallic wire or rod, discharge occurs in the form of an exceedingly bright spark, accompanied by a loud snap; and if the human body be interposed in the circuit, the peculiar and disagreeable sensation of the electric shock is felt at the moment of its completion.

By enlarging the dimensions of the jar, or by connecting together a number of such jars in such a manner that all may be charged and discharged simultaneously, the power of the apparatus may be greatly augmented. Thin wires of metal may be fused and dissipated; pieces of wood may be shattered; many combustible substances set on fire; and all the well-known effects of lightning exhibited upon a small scale.

The electric spark is often very conveniently employed in chemical inquiries for firing gaseous mixtures in closed vessels. A small Leyden jar charged by the machine is the most effective contrivance for this purpose; but, not unfrequently, a method may be resorted to which involves less preparation. This method was devised by Bunsen. A large porcelain tube, which is dry and warm, is wrapped round and rubbed briskly by a dry silken cloth, and after each rub, the tube is brought in the immediate neighborhood of the knob of a small Leyden jar, the outer coating of this vessel being in connection with the earth.

The electrophorus (fig. 62) is also frequently used for this purpose. This instrument consists of a round tray or dish of tinned plate, having a stout wire round its upper edge; the width may be about twelve inches,

Fig. 62.



and the depth half an inch. This tray is filled with melted shellac, and the surface rendered as even as possible. A brass disk, with rounded edge, of about nine inches diameter, is also provided, and fitted with an insulating handle. The resinous plate is excited by striking it with a dry, warm piece of fur or flannel, whereby it becomes charged with negative electricity. If the cover be then placed upon it, the positive electricity is drawn to the under surface of the metal nearest to the negatively charged resinous

cake, while the negative electricity is repelled to the upper surface of the cover; on touching the cover with the finger, the negative electricity passes away to the earth, while an additional quantity of positive electricity is drawn into the plate; and if the finger be removed and the cover then lifted by its insulating handle, it will be found so strongly charged by induction with positive electricity as to give a bright spark; and as the resin is not discharged by the cover, which merely touches it at a few points, sparks may be drawn as often as may be wished.

Atmospheric Electricity.—It is not known to what cause the disturbance of the electrical equilibrium of the atmosphere is due; experiment has shown that the higher regions of the air are usually in a positive state, the intensity of which reaches a maximum at a particular period of the day. In cloudy and stormy weather the distribution of the atmospheric electricity becomes much deranged, clouds near the surface of the earth often appearing in a negative state.

The circumstances of a thunder-storm exactly resemble those of the charge and discharge of a coated plate or jar; the cloud and the earth represent the two coatings, and the intervening air the bad conducting body, or *dielectric*. The polarities of the opposed surface and of the insulating medium between them become raised by mutual induction, until violent disruptive discharge takes place through the air itself, or through any other bodies which may happen to be in the interval. When these are

capable of conducting freely, the discharge is silent and harmless; but in other cases it often proves highly destructive. These dangerous effects are now in a great measure obviated by the use of lightning-rods attached to buildings, the erection of which, however, demands a number of precautions not always understood or attended to. The masts of ships may be guarded in like manner by metal conductors. Sir W. Snow Harris has devised a most ingenious plan for the purpose, which is now adopted, with complete success, in the Royal Navy.

The electricity exhibited under certain circumstances by a jet of steam, first observed by mere accident, but since closely investigated by Sir W. Armstrong, and afterwards by Faraday, is now referred to the friction, not of the pure steam itself, but of particles of condensed water, against the interior of the exit-tube. It has been proved with certainty, within the last few years, that evaporation alone is not capable of disturbing the electrical equilibrium, and the hope first entertained, that these phenomena would throw light upon the cause of electrical excitement in the atmosphere, is now abandoned. The steam is usually positive if the jet-pipe be constructed of wood or clean metal, but the introduction of the smallest trace of oily matter causes a change of sign. The intensity of the charge is, *contra predicta*, increased with the elastic force of the steam. By this means effects have been obtained very far surpassing those of the most powerful plate electrical machines ever constructed.

Although no electricity can be directly evolved by evaporation, yet vapor possesses in a high degree the property of discharging into the atmosphere that electricity which often accumulates in bodies from which it arises. The fresh branches and leaves of trees do this to the greatest extent. When moistened with rain or dew, their surfaces become positively electrical, whilst the internal parts, even to the roots, become negatively electrical.

ELECTRIC CURRENT; ELECTRIC BATTERY.

When two solid conducting bodies are plunged into a liquid which acts upon them unequally, the electric equilibrium is disturbed, the one acquiring the positive condition, and the other the negative. Thus, pieces of zinc and platinum put into dilute sulphuric acid, constitute an arrangement capable of generating electrical force: the zinc, which is the metal attacked, becomes negative; the platinum, which remains unaltered, assumes the positive condition; and on making a metallic communication in any way between the two plates, discharge ensues, as when the two surfaces of a coated and charged jar are put into connection.

No sooner, however, has this occurred, than the disturbance is repeated; and as these successive charges and discharges take place through the fluid and metals with inconceivable rapidity, the result is an apparently continuous action, to which the term *electrical current* is given.

It is necessary to guard against the idea, which the term naturally suggests, of an actual bodily transfer of something through the substance of the conductors, like water through a pipe; the real nature of all these phenomena is entirely unknown; the expression is convenient notwithstanding, and consecrated by long use; and with this caution, the very dangerous error of applying figurative language to describe an effect, and even seeking the nature of the effect from the common meaning of words, may be avoided.

The intensity of the electrical excitement developed by a single pair of metals and a liquid is too feeble to affect the most delicate gold-leaf electrometer; but, by arranging a number of such alternations in a connected series, in such a manner that the direction of the current shall be the

same in each, the intensity may be very greatly exalted. The instruments invented by Volta, called the pile and crown of cups, depend upon this principle.

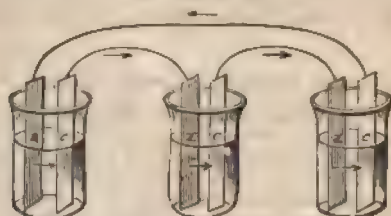
Upon a plate of zinc is laid a piece of cloth, rather smaller than itself, steeped in dilute acid, or any liquid capable of exerting chemical action upon the zinc; upon this is placed a plate of copper, silver, or platinum; then a second piece of zinc, another cloth, and a plate of inactive metal, until a pile of about twenty alternations has been built up. If the two terminal plates be now touched with wet hands, the sensation of the electrical shock will be experienced; but, unlike the momentary effect produced by the discharge of a jar, the sensation can be repeated at will by repeating the contact, and with a pile of one hundred such pairs, excited by dilute acid, it will be nearly insupportable. When such a pile is insulated, the two extremities exhibit strong positive and negative states; and when connection is made between them by wires armed with points of hard charcoal or plumbago, the discharge takes place in the form of a bright, enduring spark or stream of fire.

Fig. 63.



The second form of apparatus, or crown of cups, is precisely the same in principle, although different in appearance. A number of cups or glasses are arranged in a row or circle, each containing a piece of active and a piece

Fig. 64.



of inactive metal, and a portion of exciting liquid—zinc, copper, and dilute sulphuric acid, for example. The copper of the first cup is connected with the zinc of the second, the copper of the second with the zinc of the third, and so to the end of the series. On establishing a communication between the first and last plates by means of a wire, or otherwise, discharge takes place as before.

When any such electrical arrangement consists merely of a single pair of conductors and an interposed liquid, it is called a "simple circuit;" when two or more alternations are concerned, the term "compound circuit" is applied: they are called also, indifferently, Voltaic batteries. In every form of such apparatus, however complex it may appear, the direction of the current may be easily understood and remembered.

When both ends of the series are insulated, the zinc end exhibits negative, the copper or platinum end positive electricity; consequently, when the two extremities or poles are joined by a conducting wire and a complete circuit formed, the current of positive electricity proceeds *without* the battery from the platinum or copper to the zinc, and *within* the battery, from the zinc to the copper or platinum, as indicated by the arrows—just as in the common electrical machine, when the positive conductor and the rub-

ter are joined by a wire, the positive current proceeds from the conductor through the wire to the rubber, and thence along the surface of the glass cylinder or plate to the conductor again.

In the construction of Volta's original pile, made by Croikshank, the zinc and copper plates are soldered together, and cemented water-tight into a mahogany trough, which thus becomes divided into a series of cells or compartments capable of receiving the exciting liquid. This apparatus (fig. 65) is well fitted to exhibit effects of *tension*, to act upon the electro-

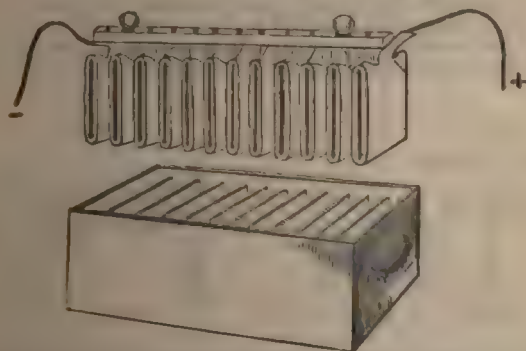
Fig. 65.



scope, and give shocks: hence its advantageous employment in the application of electricity to medicine.

A form of battery more convenient for most purposes is that contrived by Volta (fig. 66). In this the copper is made completely to encircle the zinc plate, except at the edges, the two metals being kept apart by pieces of cork or wood. Each zinc is soldered to the preceding copper, and the whole screwed to a bar of dry mahogany, so that the plates can be lifted into or out of the acid, which is contained in an earthenware trough, divided into separate cells. The liquid consists of a mixture of 100 parts water, $2\frac{1}{2}$ parts oil of vitriol, and 2 parts commercial nitric acid, all by measure. A number of such batteries are easily connected together by straps of sheet copper, and admit of being put into action with great ease.

Fig. 66.



In all these older forms of the voltaic battery, however, the power rapidly diminishes, so that, after a short time, scarcely the tenth part of the original action remains. This loss of power depends partly on the gradual change of the sulphuric acid into zinc sulphate, but still more on other causes, which, together with the more modern forms of the battery which have been contrived to obviate them, will be more easily understood at a subsequent part of the work, when we come to consider the nature and effects of *electro-chemical decomposition*.

The term "galvanism," sometimes applied to this branch of electrical science, is used in honor of Galvani, of Bologna, who, in 1790, made the very curious observation that convulsions could be produced in the limbs of a dead frog when certain metals were made to touch the nerve and muscle at the same moment. It was Volta, however, who pointed out the electrical origin of these motions; and although the explanation he offered of the source of the electrical disturbance is no longer generally adopted, his name is very properly associated with the invaluable instrument his genius gave to science.

ELECTRO-MAGNETISM.

Although the fact that electricity is capable, under certain circumstances, both of inducing and of destroying magnetism, has long been known from the effects of lightning on the compass-needle and upon small steel articles, as knives and forks, to which polarity has suddenly been given by the stroke, it was not until 1819 that the laws of these phenomena were discovered by Oersted, of Copenhagen, and shortly afterwards fully developed by Ampère.

If a wire conveying an electrical current be brought near a magnetic needle, the latter will immediately alter its position, and assume a new one as nearly perpendicular to the wire as the mode of suspension and the magnetism of the earth will permit. When the wire, for example, is placed directly over the needle, and parallel to its length, while the current it carries travels from north to south, the needle is deflected from its ordinary direction, and the north pole driven to the eastward. When the current is reversed, the same pole deviates to an equal amount towards the west. Placing the wire below the needle instead of above produces the same effect as reversing the current.

The direction which the needle will assume when placed in any particular position to the conducting wire may be determined by the following rule: *Let the current be supposed to pass through a watch from the face to the back: the motion of the north pole will be in the direction of the hands. Or, let the observer imagine himself swimming in the direction of the current with his face towards the needle: the north pole of the needle will then be deflected towards his left hand.*

Fig. 67.



Fig. 68.



If reference is often required, a little piece of apparatus (fig. 68) may be used, consisting of a piece of pasteboard, or other suitable material, cut into the form of an arrow for indicating the current, crossed by a magnet having its poles marked, and arranged in the true position with respect to the current. The direction of the latter in the wire of the galvanoscope can at once be known by placing the representative magnet in the direction assumed by the needle itself.

When the needle is subjected to the action of two currents in opposite directions, the one above and the other below, they will obviously concur

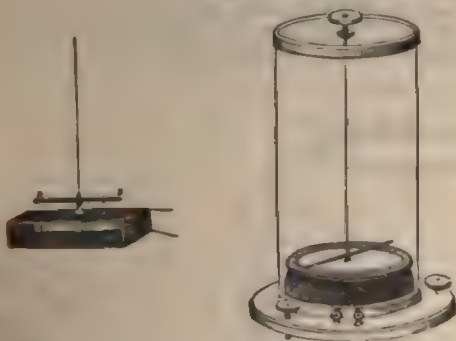
in their effects. The same thing happens when the wire carrying the current is bent upon itself, and the needle placed between the two portions as in fig. 69; and since every time the bending is repeated, a fresh portion of the current is made to act in the same manner upon the needle, it is easy to see how a current, too feeble to produce any effect when a simple straight wire is employed, may be made by this contrivance to exhibit a powerful action on the magnet. It is on this principle that instruments called *galvanometres*, *amalgams*, or *multiplicators*, are constructed; they serve not only to indicate the existence of electrical currents, but to show, by the effects upon the needle, the direction in which they are moving.

The delicacy of the instrument may be immensely increased by the use of a very long coil of wire, and by the addition of a second needle. The two needles are of equal size, and magnetized as nearly as possible to the same extent; they are then immovably fixed together parallel, and with their poles opposed, and hung by a long fibre of untwisted silk, with the lower needle in the coil, and the upper one above it. The advantage thus gained is twofold; the system is *astatic*, unaffected, or nearly so, by the magnetism of the earth; and the needles, being both acted upon in the same manner by the current, are urged with much greater force than one alone could be, all the actions of every part of the coil being strictly concurrent. A divided circle is placed below the upper needle, by which the angular motion can be measured, and the whole is inclosed in glass, to shield the needles from the agitation of the air. The arrangement is shown in fig. 70.

Fig. 69.



Fig. 70.



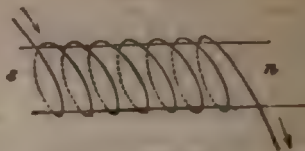
The direction of the current which deflects the galvanometer-needle in a particular way is easily determined by the rules given on page 112, when we know the direction in which the wire is coiled round the frame. For this purpose it is necessary to distinguish between *right-handed* and *left-handed* coils or helices. Suppose the wire to be coiled round a cylinder beginning at the left hand; then if the turns in front of the cylinder proceed from below upwards, as in fig. 71, the coil is left-handed; if, on the contrary, they proceed in front from above downwards, as in fig. 72, the coil is right-handed.

A magnetic needle, placed with its centre in the axis of such a coil, turns its north or south pole towards the end of the coil at which the current enters, according as the coil is left- or right-handed.

Fig. 71.



Fig. 72.



The direction given to the needle is the same whether the coil is elongated, as in the above figures, or compressed, as in the galvanometer. As, however, in the galvanometer, when complete, it is not easy to see whether the coil is left- or right-handed, it is best to determine by experiment, once for all, the direction taken by the needle when the current enters at one particular end of the coil.

Action of the Magnet on the Electric Current.—The action between the current and the magnet is mutual, so that if the conductor conveying the current is free to move, it is deflected in the direction opposite to that which the magnet takes under its influence; in short, if the magnet and conducting wire are both free to move, they place themselves at right angles to each other, the magnet moving in the manner indicated at page 112, and the wire in the opposite direction.

The action of the magnet on the current may be shown by means of Ampère's apparatus (fig. 73). On holding a bar-magnet below the rectangular wire, and parallel to its lower horizontal arm, the wire turns round and places itself at right angles to the magnet, the position of equilibrium being determined by the rule just alluded to.

Fig. 73.

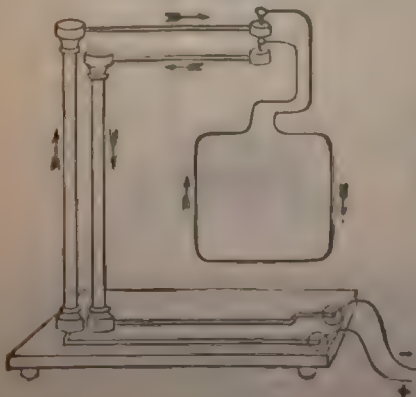
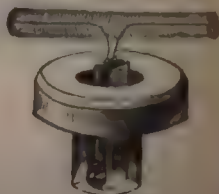


Fig. 74.



A simpler apparatus for the purpose is De la Rive's floating battery, which consists of a pair of zinc and copper plates, contained in a wide

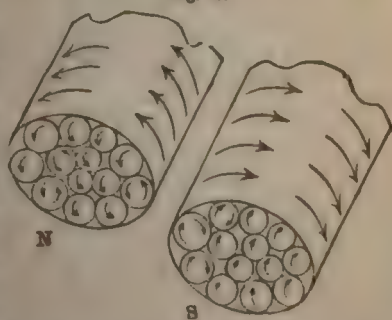
glass tube attached to a cork float, and connected together by a rectangular wire, or a flat coil, or elongated helix of covered wire (fig. 74).

A movable electric current is deflected by the earth's magnetism in the same way as by an ordinary magnet. Thus the rectangular wire of Ampère's apparatus, or of a floating battery, when left to itself, will take up a position at right angles to the magnetic meridian; and remembering that the north magnetic pole of the earth is analogous to the south pole of an ordinary magnet, it is easy to see that, in the position of stable equilibrium, the direction of the current will be from east to west in the lower horizontal branch, and from below upwards on the western vertical side. If the wire has the form of a long helix, it will, in like manner, place itself with the turns of the helix at right angles to the magnetic meridian, and therefore with its axis parallel to that meridian, the ends pointing north and south, just like those of an ordinary magnetic needle. If the helix is left-handed, the end connected with the copper plate of the battery will point to the north.

Mutual Action of Electric Currents.—If a conducting wire, connecting the poles of a voltaic battery, be brought near the movable wire of Ampère's apparatus, or the wire of a floating battery, the movable wire will be attracted or repelled according to the relative direction of the two currents, the general law of the action being that, *electric currents moving in parallel lines attract one another if they move in the same direction, and repel one another if they move in opposite directions.* From this it is easy to see that if a helix connecting the two poles of a battery be brought near the helix of a floating battery, and if the two helices are similar—that is, both right- or both left-handed—their similar ends, *i. e.*, those by which the current enters or leaves the helix, will repel each other, and their dissimilar ends will attract each other, and consequently the movable helix will place itself parallel to the fixed helix with its poles or ends in the contrary direction to those of the fixed helix. In short, the two helices will act on one another exactly like two bar-magnets; and if an ordinary bar-magnet be substituted for the fixed helix, the effect will still be the same, each end of the movable helix being attracted by one pole of the magnet and repelled by the other.

This striking resemblance between the mutual action of electric currents and that of magnets has led to the idea, suggested and developed by Ampère, that magnetism is actually produced by electric currents circulating round the molecules of a magnet all in the same direction. These currents may be supposed to pre-exist in all magnetic bodies, even before the development of magnetic polarity, but to be disposed without regularity, so that they neutralize each other. Magnetization is the process by which these molecular currents are made to move in one direction, those situated at the surface yielding, as their resultant, a finite current circulating round the magnet, while the currents in the interior are neutralized by those in the next external layer, the contiguous portions of which move in a direction opposite to their own. The resultant action of all these molecular currents is equivalent to that of a number of currents circulating round the magnet in planes perpendicular to its

Fig. 75.

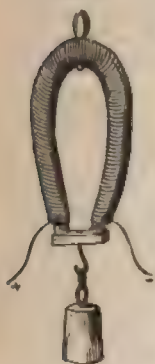


axis (fig. 75); and, from what has been said about the mutual action of magnets and helices traversed by electric currents, it is easy to see that, on looking along the axis of a magnet with its *south* pole towards the observer, the current moves in the direction of the hands of a watch, that is, upwards on the left side, and downwards on the right.

ELECTRO-DYNAMIC INDUCTION.

1. *Magnetization by the Current.*—When an electro-current is passed through a wire placed at right angles to a bar of iron or steel, the bar acquires magnetic polarity, temporary in the case of soft iron, permanent in the case of hard iron or steel, the position of the poles being determined by the direction of the current, according to the laws already explained.

Fig. 76.



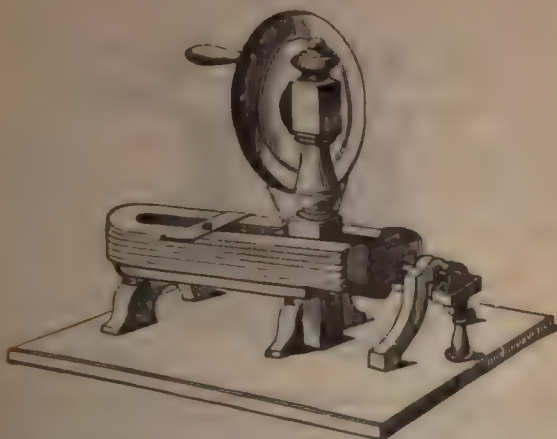
This effect is prodigiously increased by coiling the conducting wire in a helix round the bar. A piece of soft iron worked into the form of a horse-shoe (fig. 76), and surrounded by a coil of wire covered with silk or cotton for the purpose of insulation, furnishes an excellent illustration of the inductive energy of the current in this respect: when the ends of the wire are put into communication with a small voltaic battery of a single pair of plates, the iron instantly becomes so highly magnetic as to be capable of sustaining a very heavy weight.

2. *Induction of Electric Currents by the action of Magnets, and of other Electric Currents.*—If the two extremities of the coil of the electro-magnet above described be connected with a galvanoscope, and the iron magnetized by the application of a permanent steel horse-shoe magnet to the ends of the bar, a momentary current will be developed in the wire, and pointed out by the movement of the needle. It lasts but a single instant, the needle, after a few oscillations, returning to a state of rest. On removing the magnet, whereby the polarity of the iron is at once destroyed, a second current or wave will become apparent, but in the opposite direction to that of the first. By employing a very powerful steel magnet, surrounding its iron keeper or armature with a very long coil of wire, and then making the armature itself rotate in front of the faces of the magnet, so that its induced polarity shall be rapidly reversed, magneto-electric currents may be produced, of such intensity as to give bright sparks and most powerful shocks, and exhibit all the phenomena of voltaic electricity. Fig. 77 represents a very powerful arrangement of this kind.

When two covered wires are twisted together or laid side by side for some distance, and a current transmitted through the one, a momentary electrical wave will be induced in the other in the reverse direction; and on breaking connection with the battery, a second single wave will become evident by the aid of the galvanoscope, in the same direction as that of the primary current. In the same way, when a current of electricity passes through one turn in a coil of wire, it induces two secondary currents in all the other turns of the coil; the first current, which is induced when the circuit is closed, moves in the opposite direction to the primary current; the second, which comes in existence when the circuit is broken, has a motion in the same direction as the primary current. The effect of the latter is added to that of the primary current. Hence, if a wire coil be made part of the conducting wire of a weak electric pile, and if the primary current, by means of an appropriate arrangement, be made and broken in rapid succession, we can increase in a remarkable manner the

effects which are produced at the moment of breaking the circuit, either at the place of interruption, such as the spark-discharges, or in secondary closing conductors, as in the action on the nerves, or in the decomposition of water.

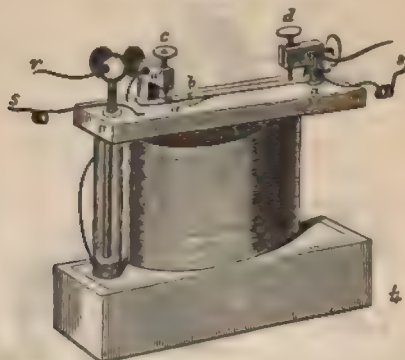
Fig. 77.



If the two copper wires, the one above the other, be twisted round the same hollow cylinder, and one of these wires—the inner one, for instance—be made part of a galvanic circuit, a current of short duration is induced in the outer wire, both by making and by breaking contact. The strength of this current can be very appreciably increased by filling the hollow cylinder with a bundle of thin iron rods, whereby magnetic and electrical induction are made to co-operate. The more frequently contact is alternately made and broken, the greater is the number of induced currents that follow each other, and the more powerful, within certain limits, is the action. By an ingenious contrivance, the invention of Dr. Neef, in which contact is made and broken by the current itself, the induction apparatus actually becomes an electrical machine. Fig. 78 exhibits the original apparatus slightly modified. The arrangement consists essentially of an elastic copper strip *a a'*, which is fixed at *a'*, and carries at *b* a small plate of soft iron. The latter hangs over the iron rods of the induction coil, which are somewhat raised in this particular point, but without touching them. The end *a* of the copper strip is covered with a little plate of platinum, which presses against a platinum point of the screw *c*. The current, having traversed the inner coil, passes from the point *c* to the plate *a*, in order to return through the copper strip *a a'* and the wire *a*. By the passage of the current the iron rods have become magnetic and attract the iron plate *b*, whereby the end *a* of the copper strip is removed from the platinum point, and contact is broken. But as soon as the current ceases, the iron rods lose their magnetism, the elastic copper strip returns to its former position, and establishes again the current for a short time. The screws *c* and *d* regulate the position of the spring and the time of its oscillations, the velocity of which may be estimated by the pitch of the notes produced. This apparatus, called an induction coil, which was first made by Dr. Neef, in 1830, has been considerably improved within

the last few years. Ruhmkorff especially, by a more perfect isolation of the wire coils, has succeeded to a much greater extent in preserving the electrical induction. He has thus obtained a state of electrical tension which resembles that produced by frictional electricity, capable of giving

Fig. 78.



long sparks, and shocks of unendurable force. By means of Ruhmkorff's coil, Grove has effected decompositions in water and other bad-conducting liquids, which resemble those obtained many years ago by Wollaston by means of the electrical machine. These phenomena of decomposition, which in water, for instance, furnish oxygen and hydrogen at the same pole, must be distinguished from true electro-chemical decompositions; they are, in fact, effects of heat, as Grove has pointed out.

THERMO-ELECTRICITY.

In the year 1822 Professor Seebeck of Berlin discovered a new source of electricity, namely, inequality of temperature and conducting power in different metals placed in contact, or in the same metal in different states of compression and density.

Where two pieces of different metals, connected together at each end, have one of their joints more heated than the other, an electric current is immediately set up. Of all the metals tried, bismuth and antimony form

Fig. 79.

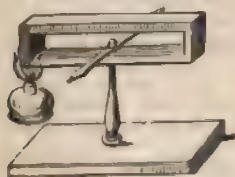


Fig. 80.



the most powerful combination. A single pair of bars having one of their junctions heated in the manner shown in fig. 79 can develop a current

strong enough to deflect a compass needle placed within; and, by arranging a number in a series and heating their alternate ends, the intensity of the current may be very much increased. Such an arrangement, represented in fig. 80, is called a thermo-electric pile.

The current produced by this instrument, even with a great number of alterations, is exceedingly feeble when compared with that produced by the voltaic pile; but the thermomultiplier placed in contact with a delicate galvanoscope forms an instrument for measuring small variations of temperature, far surpassing in delicacy the most sensitive air-thermometer; it has rendered most important service in the study of radiant heat.

ANIMAL ELECTRICITY.

Certain fishes, as the torpedo or electric ray and the electric eel (*Gymnotus electricus*), of South America, are furnished with a special organ or apparatus for developing electric force, which is employed in defence, or in the pursuit of prey. Electricity is here seen to be closely connected with nervous power; the shock is given at the will of the animal, and great exhaustion follows repeated exertion of the power.

PART II.

CHEMISTRY OF ELEMENTARY BODIES.

It is convenient for many reasons to commence the study of the elementary bodies with those which enter into the composition of air and water.

OXYGEN.

Atomic weight, 16.—Symbol, O.

Oxygen was discovered in the year 1774, by Scheele, in Sweden, and Priestley, in England, independently of each other, and described under the terms *empyreal air* and *dephlogisticated air*. The name oxygen* was given to it by Lavoisier some time afterwards. Oxygen exists in a free and uncombined state in the atmosphere, mixed with another gaseous body, nitrogen. No very good direct means exist, however, for separating it from the latter; and, accordingly, it is always obtained for purposes of experiment by decomposing certain of its compounds, which are very numerous.

The red oxide of mercury, or *red precipitate* of the old writers, may be employed for this purpose. In this substance the attraction which holds together the mercury and the oxygen is so feeble, that simple exposure to heat suffices to bring about decomposition.

The red precipitate is placed in a short tube of hard glass, to which is fitted a perforated cork, furnished with a piece of narrow glass tube, bent as in fig. 81. The heat of a spirit lamp being applied to the substance, decomposition speedily commences, and globules of metallic mercury collect in the cool part of the wide tube, which answers the purpose of a retort, while gas issues in considerable quantity from the apparatus. This gas is collected and examined by the aid of the pneumatic trough, which consists of a vessel of water provided with a shelf, upon which stand the jars or bottles destined to receive the gas, filled with water and inverted. By keeping the level of the liquid above the mouth of the jar, the water is retained in the latter by the pressure of the atmosphere, and entrance of air is prevented. When the jar is brought over the extremity of the gas-delivery tube, the bubbles of gas, rising through the water, collect in the upper part of the jar, and displace the liquid. As soon as one jar is filled, it may be removed, still keeping its mouth below the water-level, and another substituted. The whole arrangement is shown in fig. 81.

The experiment here described is more instructive as an instance of the resolution by simple means of a compound body into its constituents, than valuable as a source of oxygen gas. A better and more economical method is to expose to heat in a retort, or flask furnished with a bent tube, a portion of the salt called potassium chlorate. A common Florence flask serves perfectly well, the heat of the spirit-lamp being sufficient. The salt melts and decomposes with ebullition, yielding a very large quantity of oxygen

* From $\acute{o}\pi\eta\sigma$, acid, and $\gamma\epsilon\gamma$ a root signifying production.

gas, which may be collected in the way above described. The first portion of the gas often contains a little chlorine. The white saline residue in the flask is potassium chloride. This plan, which is very easy of execution, is always adopted when very pure gas is required for analytical purposes.

Fig. 61.



A third method, very good when perfect purity is not demanded, is to heat to redness, in an iron retort or gun-barrel, the black manganese oxide of commerce, which under these circumstances suffers decomposition, although not to the extent manifest in the red precipitate.

If a little of the black manganese oxide be finely powdered and mixed with potassium chlorate, and this mixture heated in a flask or retort by a lamp, oxygen will be disengaged with the utmost facility, and at a far lower temperature than when the chlorate alone is used. All the oxygen comes from the chlorate, the manganese remaining quite unaltered. The materials should be well dried in a capsule before their introduction into the flask. This experiment affords an instance of an effect by no means rare, in which a body seems to act by its mere presence, without taking any obvious part in the change brought about.

Methods for the preparation of oxygen on a large scale will be found described under the heads of sulphuric acid and barium dioxide.

Whatever method be chosen—and the same remark applies to the collection of all other gases by similar means—the first portions of gas must be suffered to escape, or be received apart, as they are contaminated by the atmospheric air of the apparatus.

The practical management of gases is a point of great importance to the chemical student, and one with which he must endeavor to familiarize himself. The water-trough just described is one of the most indispensable articles of the laboratory, and by its aid all experiments on gases are carried on when the gases themselves are not sensibly acted upon by water. The trough is best constructed of japanned copper, the form and dimensions being regulated by the magnitude of the jars. It should have a firm shelf, so arranged as to be always about an inch below the level of the water, and in the shelf a groove should be made about half an inch in width, and the same in depth, to admit the extremity of the delivery-tube beneath the jar, which stands securely upon the shelf. When the

Fig. 82.

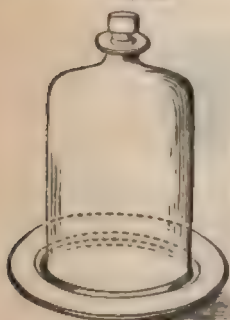


pneumatic trough is required of tolerably large dimensions, it may with great advantage have the form and dispositions represented in fig. 82. The end of the groove spoken of, which crosses the shelf or shallow portion, is shown at *a*.

Gases are transferred from jar to jar with the utmost facility, by first filling the vessel, into which the gas is to be passed, with water, inverting it, carefully retaining its mouth below the water level, and then bringing

beneath it the aperture of the jar containing the gas. On gently inclining the latter, the gas passes by a kind of inverted decantation into the second vessel. When the latter is narrow, a funnel may be placed loosely in its neck, by which loss of gas will be prevented.

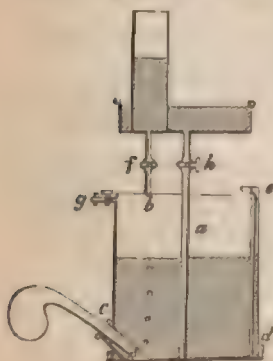
Fig. 83.



A jar wholly or partially filled with gas at the pneumatic trough may be removed by placing beneath it a shallow basin, or even a common plate, so as carry away enough water to cover the edge of the jar; and many gases, especially oxygen, may be so preserved for many hours without material injury.

Gas-jars are often capped at the top, and fitted with a stopcock for transferring gas to bladders or caoutchouc bags. When such a vessel is to be filled with water, it may be slowly sunk in an upright position in the well of the pneumatic trough, the stopcock being open to allow the air to escape, until the water reaches the brass cap. The cock is then to be turned, and the jar lifted upon the shelf, and filled with gas in the usual way. If the trough be not deep enough for this method of

Fig. 84.



proceeding, the mouth may be applied to the stopcock, and the vessel filled by sucking out the air until the water rises to the cap. In all cases it is proper to avoid as much as possible wetting the stopcocks and other brass apparatus.

Mr. Pepys contrived many years ago an admirable piece of apparatus for storing and retaining large quantities of gas. It consists of a drum or reservoir of sheet copper, surmounted by a shallow trough or cistern, the communication between the two being made by a couple of tubes furnished with stopcocks, one of which passes nearly to the bottom of the drum, as shown in fig. 84. A short wide open tube is inserted obliquely near the bottom of the vessel, into which a plug may be tightly screwed. A stopcock near the top serves to transfer gas to a bladder or tube appa-

radius. A glass water-gauge affixed to the side of the drum, and communicating with both top and bottom, indicates the level of the liquid within.

To use the gas-holder, the plug is first to be screwed into the lower opening, and the drum completely filled with water. All three stopcocks are then to be closed and the plug removed. The pressure of the atmosphere retains the water in the gas-holder, and, if no air-leakage occurs, the escape of water is inconsiderable. The extremity of the delivery-tube is now to be well pushed through the open aperture into the drum, so that the bubbles of gas may rise without hindrance to the upper part, displacing the water, which flows out in the same proportion into a vessel placed for its reception. When the drum is filled, or enough gas has been collected, the tube is withdrawn and the plug screwed into its place.

When a portion of the gas is to be transferred to a jar, the latter is to be filled with water at the pneumatic trough, carried by the help of a basin or plate to the cistern of the gas-holder, and placed over the shorter tube. On opening the cock of the neighboring tube, the hydrostatic pressure of the column of water will cause compression of the gas, and increase its elastic force, so that, on gently turning the cock beneath the jar, it will ascend into the latter in a rapid stream of bubbles. The jar, when filled, may again have the plate slipped beneath it, and be removed without difficulty.

Fig. 85.



Properties of Oxygen.—Oxygen, when free or uncombined, is known only in the gaseous state, all attempts to reduce it to the liquid or solid condition by cold and pressure having completely failed.* When pure, it is colorless, tasteless, and inodorous.

Oxygen is, bulk for bulk, a little heavier than atmospheric air, its specific gravity being 1.10563, referred to that of air as unity, and 16 referred to that of hydrogen as unity. A litre of oxygen at the standard temperature and pressure, that is to say, at 0°C ., and 760 millimetres barometrical pressure, weighs 1.43028 gram. At 15.5°C . (60°F .), and under a pressure of 30 inches, 100 cubic inches of the gas weigh 34.29 grains.

Oxygen is the sustaining principle of animal life, and of all the ordinary phenomena of combustion. Bodies which burn in the air, burn with greatly increased splendor in oxygen gas. If a taper be blown out, and then introduced while the wick remains red hot, it is instantly rekindled: a slip of wood or a match is relighted in the same manner. This effect is highly characteristic of oxygen, there being but one other gas which possesses the same property; and this is easily distinguished by other means. The experiment with the match is also constantly used as a rude test of the purity of the gas when it is about to be collected from the retort, or when it has stood for some time in contact with water exposed to air.

When a bit of charcoal is affixed to a wire, and plunged with a single point red hot into a jar of oxygen, it burns with great brilliancy, throwing off beautiful scintillations, until, if the oxygen be in excess, it is completely consumed. An iron wire, or, still better, a steel watch-spring, armed at its extremity with a bit of lighted amadou, and introduced into a vessel of oxygen gas, exhibits a most beautiful phenomenon of combustion. If the experiment be made in a jar standing on a plate, the fused globules of black iron oxide fix themselves in the glaze of the latter, after rising through a stratum of water half an inch in depth. Kindled sulphur burns with great beauty in oxygen; and phosphorus, under similar

* It has been lately announced that M. Raoul Pictet, of Geneva, has succeeded in reducing oxygen to the liquid state by cold and intense pressure.—R. B.

circumstances, exhibits a splendor which the eye is scarcely able to support. In each case the burning body enters into combination with the oxygen, forming a compound called an oxide.

When a body burns in oxygen gas the same ultimate effect is produced as in atmospheric air; the action is, however, more energetic, from the absence of the gas which, in the air, dilutes the oxygen and enfeebles its chemical powers. The process of respiration in animals is an effect of the same nature as common combustion. The blood contains substances which slowly burn by the aid of the oxygen thus introduced into the system. When this action ceases, life becomes extinct.

Ozone.—It has long been known that dry oxygen, or atmospheric air, when exposed to the action of a series of electric sparks, emits a peculiar and somewhat metallic odor. The same odor may be imparted to moist oxygen by allowing phosphorus to remain for some time in it, and by several other processes. A more accurate examination of this odorous air has shown that, in addition to the smell, it possesses several properties not exhibited by oxygen in its ordinary state. One of its most characteristic effects is the liberation of iodine from potassium iodide. This odorous principle has been the subject of many researches, in particular by Schönbein, of Basle, who proposed for it the name of *ozone*.*

An easy method of exhibiting the production of ozone is to transmit a current of oxygen through a tube into which a pair of platinum wires is sealed, with the points at a little distance apart; on connecting one of the wires with the prime conductor of an electrical machine in good action, and the other with the ground, the characteristic odor of ozone is immediately developed in the issuing gas; but, notwithstanding the powerful odor thus produced, only a small portion of the oxygen undergoes this change. Andrews and Tait have shown that, to obtain the maximum of ozone, it is necessary to transmit the discharge silently, between very fine points; if sparks are allowed to pass, a considerable portion of the ozone is reconverted into ordinary oxygen as fast as it is formed. Siemens prepares ozone by induction: he forms a sort of Leyden jar, by coating the interior of a long tube with tinfoil, and passes over this tube a second water tube, coated with tinfoil on its outer surface. Between the two tubes a current of pure dry oxygen is passed, which becomes electrified by induction, on connecting the inner and outer coating with the terminal wires of an induction-coil, by this means it is said that from 10 to 15 per cent. of the oxygen may be converted into ozone.

Ozone may also be obtained in several ways, without the aid of electricity, thus it is formed in small quantity when a stick of phosphorus is suspended in a bottle filled with moist air; in the electrolytic decomposition of water; and by the action of strong sulphuric acid on potassium permanganate. There has been considerable discussion about the nature and composition of ozone; but the most trustworthy experiments seem to show that, in whatever way produced, it is merely a modified form of oxygen.

Ozone is insoluble in water and in solutions of acids or alkalies, but it is absorbed by a solution of potassium iodide. Air charged with it exerts an irritating action on the lungs. Ozone is decomposed by heat, gradually at 100° (212° F.), instantly at 200° (354° F.). It is an extremely powerful oxidizing agent; possesses strong bleaching and disinfecting powers; corrodes cork, caoutchouc, and other organic substances; and rapidly oxidizes iron, copper, and even silver when moist, as well as dry mercury and iodine. It is remarkable that the absorption of ozone by these and other agents is not attended with any contraction of volume. The explanation of this fact

* From *Ozōn*, to emit an odor.

appears to be that oxygen, when ozonized, diminishes in volume (in the proportion of 3 to 2, according to Serret), and that when the ozone is decomposed by a metal or other substance, one portion of it enters into combination, while the remainder, which is set free as ordinary oxygen, occupies the same bulk as the ozone itself.

The most delicate test for the presence of ozone in any gas is afforded by a strip of paper moistened with a mixture of starch and solution of potassium iodide. On exposing such paper to the action of ozone, the potassium iodide is decomposed, its potassium combining with oxygen, while the iodine is liberated, and forms a deep blue compound with the starch. Now, when paper thus prepared is exposed to the open air for five or ten minutes, it often acquires a blue tint, the intensity of which varies on different days. Hence, it is supposed that ozone is present in the air in variable quantity. But iodine may be liberated from potassium iodide by many other agents, especially by certain oxides of nitrogen, which are very likely to be present in the air in minute quantities: hence, the existence of ozone in the air cannot be proved by this reaction alone.

Houzeau has, however, shown that a solution of potassium iodide exposed to the air in the open country becomes alkaline; an effect which cannot be attributed to nitrous acid. Moreover, Andrews finds that the constituent of the air which separates iodine from potassium iodide is destroyed by the same influences as ozone, viz., by a temperature of 237° (458° F.), or by contact with manganese dioxide and other peroxides. The presence of ozone in the air can therefore no longer be doubted.

Oxides—General Laws of Chemical Combination.—Chemical Nomenclature and Notation.—The compounds formed by the union of oxygen with other bodies bear the general name of oxides; they are very numerous and important. They are conveniently divided into three principal groups or classes. The first division contains all those oxides which resemble in their chemical relations the oxides of potassium, sodium, silver, or lead: these are denominated alkaline or basic oxides. The oxides of the second group have properties opposed to those of the bodies mentioned; the oxides of sulphur and phosphorus may be taken as typical representatives of the class; they are called acid oxides, and are capable of uniting with the basic oxides, and forming compounds called salts. Thus, when the oxide of sulphur, called sulphuric oxide, is passed in the state of vapor over heated barium oxide, combination takes place, attended with vivid incandescence, and a salt called barium sulphate is produced, containing all the elements of the two original bodies, namely, barium, sulphur, and oxygen.

There is also an intermediate group of oxides called neutral oxides, from their slight disposition to enter into combination. The black oxide of manganese, already mentioned, is an excellent example. It must not be supposed, however, that the three groups of oxides just mentioned are separated from each other by decided lines of demarcation; on the contrary, they blend into one another by imperceptible degrees, and the same oxide may, in many cases, exhibit either acid or basic relations, according to the circumstances under which it is placed.

Among salts there is a particular group, namely, the hydrogen salts, containing the elements of an acid oxide and water (hydrogen oxide), which are especially distinguished as acids, because many of them possess in an eminent degree the properties to which the term acid is generally applied, such as a sour taste, corrosive action, solubility in water, and the power of reddening certain blue vegetable colors. A characteristic property of these acids, or hydrogen salts, is their power of exchanging their hydrogen for a metal presented to them in the free state, or in the form of

oxide. Thus, sulphuric acid, which contains sulphur, oxygen, and hydrogen, readily dissolves metallic zinc, the metal taking the place of the hydrogen, which is evolved as gas, and forming a salt containing sulphur, oxygen, and zinc; in fact, a *zinc sulphate*, produced from a *hydrogen sulphate* by substitution of zinc for hydrogen. The same substitution and formation of zinc sulphate take place when zinc oxide is brought into contact with sulphuric acid; but in this case the hydrogen, instead of being evolved as gas, remains combined with the oxygen derived from the zinc oxide, forming water.

A series of oxides containing quantities of oxygen in the proportion of the numbers 1, 2, 3, united with a constant quantity of another element, are distinguished as *monoxide*, *dioxide*, and *trioxide* respectively, the Greek numerals indicating the several degrees of oxidation. A compound, intermediate between a monoxide and a dioxide is called a *sesquioxide*, *e. g.* :—

| | Chromium. | Oxygen. |
|--------------------------------|-----------|---------|
| Chromium monoxide | 52.5 | + 16 |
| Chromium sesquioxide | 52.5 | + 24 |
| Chromium dioxide | 52.5 | + 32 |
| Chromium trioxide | 52.5 | + 48 |

When a metal forms two basic or salifiable oxides, they are distinguished by adjectival terms, ending in *ous* for the lower, and *ic* for the higher degree of oxidation, *e. g.* :—

| | Iron. | Oxygen. |
|---|-------|---------|
| Iron monoxide, or Ferrous oxide | 56 | + 16 |
| Iron sesquioxide, or Ferric oxide | 56 | + 24 |

The salt resulting from the action of acids on these oxides are also distinguished as *ferrous* and *ferric* salts respectively.

Acid oxides of the same element, sulphur for example, are also distinguished by the terminations *ous* and *ic*, applied as above; their acids, or hydrogen salts, receive corresponding names; and the salts formed from these acids are distinguished by names ending in *ite* and *ate* respectively. Thus, for the oxides and salts of sulphur :—

| | Sulphur. | Oxygen. | |
|---|----------|---------|------------------|
| Sulphurous oxide | 32 | + 32 | |
| Hydrogen sulphite, or Sulphurous acid | 32 | + 48 | Hydrogen.
2 |
| Lead sulphite | 32 | + 48 | + Lead.
207 |
| Sulphuric oxide | 32 | + 48 | |
| Hydrogen sulphate, or Sulphuric acid | 32 | + 64 | + Hydrogen.
2 |
| Lead sulphate | 32 | + 64 | + Lead.
207 |

The acids above spoken of are oxygen acids; and formerly it was supposed that all acids contained oxygen—that element being, indeed, regarded as the acidifying principle: hence its name (*p.* 120). At present, however, we are acquainted with many bodies which possess all the characters above specified as belonging to an acid, and yet do not contain oxygen. For example, hydrochloric acid (formerly called *muratic acid*, or *spirit of salt*)—which is a hydrogen chloride or compound of hydrogen and chlorine—is intensely sour and corrosive; reddens litmus strongly; dissolves zinc, which drives out the hydrogen and takes its place in combination with the chlorine, forming zinc chloride; and dissolves most metallic oxides, exchanging its hydrogen for the metal, and forming a metallic chloride and water.

Bromine, iodine, and fluorine, also form, with hydrogen, acid compounds analogous in every respect to hydrochloric acid.

Compounds of chlorine, bromine, iodine, fluorine, sulphur, selenium, phosphorus, etc., with hydrogen and metals, are grouped, like the oxygen-compounds, by names ending in *ide*: thus we speak of zinc chloride, calcium fluoride, hydrogen sulphide, copper phosphide, etc. The numerical prefixes, *mono*, *di*, *tri*, etc., as also the terminations *ous* and *ic*, are applied to these compounds in the same manner as to the oxides, thus—

| | Hydrogen. | Bromine. |
|-----------------------------------|------------|-----------|
| Hydrogen bromide | 1 | + 80 |
| | Potassium. | Sulphur. |
| Potassium monosulphide | 78.2 | + 32 |
| Potassium disulphide | 78.2 | + 64 |
| Potassium trisulphide | 78.2 | + 96 |
| Potassium tetrasulphide | 78.2 | + 128 |
| Potassium pentasulphide | 78.2 | + 160 |
| | Iron. | Chlorine. |
| Ferrous chloride | 56 | + 71 |
| Ferric chloride | 56 | + 106.5 |
| | Tin. | Sulphur. |
| Stannous sulphide | 118 | + 64 |
| Stannic sulphide | 118 | + 128 |

The Latin prefixes *uni*, *bi*, *ter*, *quadro*, etc., are often used instead of the corresponding Greek prefixes; there is no very exact rule respecting their use: but, generally speaking, it is best to employ a Greek or Latin prefix, according as the word before which it is placed is of Greek or Latin origin. Thus, *dioxide* corresponds with *bisulphide*; on the whole, however, the Greek prefixes are most generally employed.

The composition of these oxides and sulphides affords an illustration of a law which holds good in a large number of instances of chemical combination, viz., that when two bodies, A and B, are capable of uniting in several proportions, the several quantities of B which combine with a given or constant quantity of A stand to one another in very simple ratios. Thus, the several quantities of sulphur which unite with a given quantity (76.2 parts) of potassium are to one another as the numbers

1, 2, 3, 4, 5;

and the quantities of oxygen which unite with a given quantity of chromium are as the numbers

1, 1½, 2, 3,
or 2, 3, 4, 6.

It must be especially observed that no compounds are known intermediate in composition between those which are represented by these numbers. There is no oxide of chromium containing $1\frac{1}{2}$ or $1\frac{2}{3}$ or $2\frac{1}{3}$ times as much oxygen as the lowest; no sulphide of potassium the quantity of sulphur in which is expressed by any fractional multiple of the lowest. The quantities of the one element which can unite with a constant quantity of the other, increase, not continuously, but by successive and well-defined steps or increments, standing to one another, for the most part, in simple numerical ratios.

This is called the "Law of Multiples." The observation of it has led to the idea that the elementary bodies are composed of ultimate or indivisible particles or atoms, each having a constant weight peculiar to

itself (the atomic weights given in the table on page 27), and that combination between two elements takes place by the juxtaposition of these atoms. A collection of elementary atoms united together to form a compound constitutes a molecule, the weight of which is equal to the sum of the weights of its component atoms. Thus an atom of chlorine weighing 35.5 unites with an atom of hydrogen weighing 1, to form a molecule of hydrogen chloride weighing 36.5. An atom of oxygen weighing 16 unites with 2 atoms of hydrogen, each weighing 1, to form a molecule of water, weighing $(16 + 2 =) 18$. An atom of oxygen, weighing 16, unites with an atom of lead, weighing 207, to form a molecule of lead oxide, weighing 223. Two atoms of potassium, each weighing 39.1, unite with 1, 2, 3, 4, and 5 atoms of sulphur, each weighing 32, to form the several sulphides enumerated on page 127.

These combinations are represented symbolically by the juxtaposition of the symbols of the elementary atoms given in the table already referred to; thus the molecule of hydrogen chloride, composed of 1 atom of hydrogen and 1 atom of chlorine, is represented by the symbol or formula HCl ; that of water (2 atoms of hydrogen and 1 atom of oxygen), by H_2O , or more shortly H_2O . In like manner the different oxides and sulphides, acids and salts above enumerated, are represented symbolically as follows:—

| | |
|--|---|
| Chromium monoxide | CrO |
| Chromium sesquioxide | CrCrOOO or Cr_2O_3 |
| Chromium dioxide | CrO_2 or CrO_2 |
| Chromium trioxide | CrOOO or CrO_3 |
| Sulphurous oxide | SOO or SO_2 |
| Hydrogen sulphite or sulphurous acid | SOOOHH or SO_3H_2 |
| Lead sulphite | SOOO Pb or SO_3Pb |
| Potassium monosulphide | KKS or K_2S |
| Potassium disulphide | KKSS or K_2S_2 |
| Potassium trisulphide | KKSSS or K_2S_3 |
| Potassium tetrasulphide | KKSSSS or K_2S_4 |
| Potassium pentasulphide | KKSSSSS or K_2S_5 |

A group of two or more atoms of the same element is denoted by placing a numeral either before the symbol, or, as in the preceding examples, a small numeral to the right of the symbol, and either above or below the line: thus OOO may be abbreviated into 3O , or O^3 , or O_3 .

The multiplication of a group of dissimilar atoms is denoted by placing a numeral to the left of the group of symbols, or by inclosing them in brackets, and placing a small numeral to the right: thus, 3HCl or $(\text{HCl})_3$, denotes 3 molecules of hydrogen chloride; $2\text{H}_2\text{SO}_4$ denotes 2 molecules of hydrogen sulphate.

The combination of two groups or molecules is denoted by placing their symbols in juxtaposition, with a dot between them: thus, ZnO.SO_3 , denotes a compound of zinc oxide with sulphur trioxide; $\text{K}_2\text{O.H}_2\text{O}$, a compound of potassium oxide with hydrogen oxide or water. Sometimes a comma or the sign $+$ is used instead of the dot. To express the multiplication of such a group, the whole is inclosed in brackets, and a numeral placed on the left: e. g., $2(\text{ZnO.SO}_3)$; $3(\text{K}_2\text{O.H}_2\text{O})$, etc. If the brackets were omitted, the numeral would affect only the symbols to the left of the dot: thus, $3\text{K}_2\text{O.H}_2\text{O}$ signifies 3 potassium oxide and 1 water, not 3 potassium oxide and 3 water.*

* The neglect of this distinction often leads to considerable confusion in chemical notation.

Equivalents.—It has been already stated that elements can replace one another in combination; thus, when hydrogen chloride is placed in contact with zinc, the zinc dissolves and enters into combination with the chlorine, while a quantity of hydrogen is evolved as gas. Now this substitution of zinc for hydrogen always takes place in definite proportion by weight, 32.6 parts of zinc being dissolved for every 1 part of hydrogen expelled. In like manner, when potassium is thrown into water, hydrogen is evolved and the potassium dissolves, 39.1 parts of the metal dissolving for every 1 part of hydrogen given off. Again, if silver be dissolved in nitric acid, and metallic mercury immersed in the solution, the mercury will be dissolved and will displace the silver, which will be separated in the metallic state; and for every 100 parts of mercury dissolved 108 parts of silver will be thrown down. In like manner, copper will displace the mercury in the proportion of 31.75 parts of copper to 100 of mercury, and iron will displace the copper in the proportion of 28 parts of iron to 31.75 parts of copper.

These are particular cases of the general law, that, *when one element takes the place of another in combination, the substitution or replacement always takes place in fixed or definite proportions.* The relative quantities of different elements which thus replace one another, are called chemical equivalents or equivalent numbers; they are either identical with the atomic weights, or simple multiples or submultiples of them. For example, in the substitution of potassium for hydrogen, and of copper for mercury, and of iron for copper, the equivalents are to one another in the same proportion as the atomic weights, as may be seen by comparing the numbers just given with those in the table on page 27. In the substitution of zinc for hydrogen, on the other hand, the quantity of zinc which takes the place of 1 part of hydrogen is only half the atomic weight; similarly in the substitution of mercury for silver.

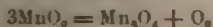
All chemical reactions consist either in the direct addition or separation of elements, or in substitutions like those just noticed, the latter being by far the most frequent form of chemical change.

Chemical Equations.—Chemical reactions may be represented symbolically in the form of equations, the symbols of the reacting substances being placed on the left hand, and those of the new substances resulting from the change, on the right: for example—

1. Resolution of mercuric oxide by heat into mercury and oxygen—



2. Resolution of manganese dioxide by heat into manganoso-manganic oxide and oxygen—



3. Action of zinc on hydrogen chloride, producing zinc chloride and free hydrogen—



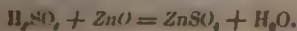
4. Action of zinc on hydrogen sulphate, producing zinc sulphate and hydrogen—



5. Action of zinc oxide on hydrogen chloride or sulphate, producing mercuric chloride or sulphate and water—



and



It need scarcely be observed that the test of correctness of such an equation is, that the number of atoms of each element on one side should be equal to the number of atoms of the same element on the other side.

Any such symbolical equation may be converted into a numerical equation, by substituting for each of the chemical symbols its numerical value from the table of atomic weights.

The laws of chemical action and their expression by symbols and equations will receive abundant illustration in the special descriptions which follow; their general consideration will also be more fully developed in a subsequent part of the work.

HYDROGEN.

Atomic weight, 1; symbol, H.

HYDROGEN may be obtained for experimental purposes by deoxidizing water, of which it forms a characteristic component.*

If a tube of iron or porcelain, containing a quantity of filings or turnings of iron, be fixed across a furnace, and its middle portion be made red-hot, and then the vapor of water passed over the heated metal, a large quantity of permanent gas will be disengaged from the tube, and the iron will be converted into oxide, and acquire an increase in weight. The gas is hydrogen; it may be collected over water and examined.

Hydrogen is, however, more easily obtained by decomposing hydrochloric or dilute sulphuric acid with zinc, the metal then displacing the hydrogen in the manner already explained (p. 129).

The simplest method of preparing the gas is the following: A wide-necked bottle is chosen, and fitted with a sound cork, perforated by two holes for the reception of a small tube-funnel reaching nearly to the bottom of the bottle, and a piece of bent glass tube to convey away the disengaged gas. Granu-

lated zinc, or scraps of the malleable metal, are put into the bottle, together

* Hence the name, *36w*, water, and *2w*.
 † A little practice will soon enable the pupil to construct and arrange a variety of useful forms of apparatus, in which bottles, and other articles always at hand, are made to supersede more costly instruments. Glass tube, purchased by weight of the maker, may be cut by scratching with a file, and then applying a little force with both hands. It may be softened and bent, when of small dimensions, by the flame of a spirit-lamp, or a candle, or, better, by a gas jet. Corks may be perforated by a heated wire, and the hole rendered smooth and cylindrical by a round file; or the ingenious cork borer of Mr. Mohr, now to be had of all instrument makers, may be used instead. Lastly, in the event of bad fitting, or unsoundness in the cork itself, a little yellow wax melted over the surface, or even a little grease applied with the finger, renders it sound and air tight, when not exposed to heat.

little water, and sulphuric acid slowly added by the funnel, the which should dip into the liquid. The evolution of gas is easily set by the supply of acid, and when enough has been discharged to the air of the vessel, it may be collected over water in a jar, or into a gas-holder. In the absence of zinc, filings of iron or small tin be used, but with less advantage.

Hydrogen is colorless, tasteless, and inodorous when quite pure. To it in this condition, it must be prepared from the purest zinc that is obtained, and passed in succession through solutions of potash and nitrate. When prepared from commercial zinc, it has a slight odor which is due to impurity, and when iron has been used, the odor is strong and disagreeable. It is inflammable, and burns, when kindled, with a pale yellowish flame, evolving much heat, but very little light.

The product of the combustion is water. Hydrogen is less soluble in water than oxygen, and has never been obtained. Although destitute of poisonous properties, it is not able of sustaining life.

Hydrogen is the lightest substance known; Dumas and Berard place its density between 0.0691 and 0.0695, as to that of air as unity. The weight of a litre of hydrogen at 0° C., and under a barometric pressure of 0.760 is 0.8961 gram; consequently a gram of hydrogen occupies a space of 11.15947 litres.* At 15.5° C. (60° F.) and the same barometric pressure, 100 cubic inches weigh 2.14

Fig 87.



as a gas is much lighter or much heavier than atmospheric air, it may often be collected and examined without the use of the pneumatic trough. A bottle or narrow jar may be filled with hydrogen without much admixture of air, by inverting it over the extremity of an upright tube delivering the gas. In a time, if the supply be copious, the air will be wholly displaced, and the jar filled. It may now be removed, the vertical position being fully retained, and closed by a stopper or a glass plate. If the mouth of the jar be wide, it must be partially closed by a piece of cardboard during the operation. This method of collecting gases by displacement is extremely useful.

Hydrogen was formerly used for filling air-balloons, being made for the purpose on the spot from zinc or iron and dilute sulphuric acid. Its use was superseded by that of coal-gas, which may be made very light by giving a high temperature in the manufacture. Although far inferior to hydrogen in buoyant power, it is found in practice to possess advantages over that substance, while its greater density is easily compensated by increasing the size of the balloon.

Mixture of Gases.—There is a very remarkable property possessed by all gases and vapors in general, which is seen in a high degree of intensity in the case of hydrogen, this is what is called diffusive power. If two different gases which do not act chemically upon each other at ordinary temperatures be connected by a narrow tube and left for some time, the gases will be found, at the expiration of a certain time, dependent upon the narrowness of the tube and its length, uniformly mixed, though they differ greatly in density, and the system has been arranged in a vertical position, with the heavier gas downwards. Oxygen and hydrogen can thus be made to mix, in a few hours, against the action of gravity, through a tube a yard in length, and not more than one-quarter

of an inch in diameter. As a near approximation, it may be remembered that a litre of hydrogen weighs 0.8961 gram, or 9 centigrams, and a gram of hydrogen occupies 11.2 litres.

of an inch in diameter: and the same is true of all other gases which are destitute of direct action upon each other.

If a vessel be divided into two portions by a diaphragm or partition of porous earthenware or dry plaster of Paris, and each half filled with a different gas, diffusion will immediately commence through the pores of the dividing substance, and will continue until perfect mixture has taken place. All gases, however, do not permeate the same porous body, or, in other words, do not pass through narrow orifices with the same degree of facility. Graham, to whom we are indebted for a very valuable investigation of this interesting subject, established the existence of a very simple relation between the rapidity of diffusion and the density of the gas, which is expressed by saying that the diffusive power varies inversely as the square root of the density of the gas itself. Thus, in the experiment supposed, if one-half of the vessel be filled with hydrogen and the other half with oxygen, the two gases will penetrate the diaphragm at very different rates; four cubic inches of hydrogen will pass into the oxygen side, while one cubic inch of oxygen travels in the opposite direction. The densities of the two gases are to each other in the proportion of 1 to 16; their relative rates of diffusion are inversely as the square roots of these numbers, *i. e.*, as 4 to 1.

In order, however, that this law may be accurately observed, it is necessary that the porous plate be very thin; with plates of stucco an inch thick or more, which really consist of a congeries of long capillary tubes, a different law of diffusion is observed.* An excellent material for diffusion experiments is the artificially compressed graphite of Mr. Brackeson, of the quality used for making writing pencils. It may be reduced by cutting and grinding to the thickness of a wafer, but still retains considerable tenacity. The pores of this substance appear to be so small as entirely to prevent the transmission of gases in mass, so that, to use the language of Mr. Graham, it acts like a molecular sieve, allowing only molecules to pass through.

The simplest and most striking method of exhibiting the phenomenon of diffusion is by the use of Graham's diffusion-tube. This is merely a piece of wide glass tube ten or twelve inches long, having one of its extremities closed by a plate of plaster of Paris about half an inch thick, and well dried. When the tube is filled by displacement with hydrogen, and then set upright in a glass of water, the level of the liquid rises in the tube so rapidly, that its movement is apparent to the eye, and speedily attains a height of several inches above the water in the glass. The gas is actually rarefied by its superior diffusive power over that of the external air.



Fig. 68.

It is impossible to overestimate the importance in the economy of Nature of this very curious law affecting the constitution of gaseous bodies: it is the principal means by which the atmosphere is preserved in a uniform state, and the accumulation of poisonous gases and exhalations in towns and other confined localities prevented.

A partial separation of gases and vapors of unequal diffusibility may be effected by allowing the mixture to permeate through a plate of graphite or porous earthenware into a vacuum. This effect, called *atmolytic*, is best exhibited by means of an instrument called the *tube atmolyzer*. This is simply a narrow tube of unglazed earthenware, such as a tobacco-pipe

* See Bunsen's *Gasometry*, p. 203; Graham's *Elements of Chemistry*, 21 ed. II. 66; *Watts's Dictionary of Chemistry*, II. 610.

feet long, which is placed within a shorter tube of glass, and in its position by corks. The glass tube is connected with an air-pump, and the annular space between the two tubes is made as nearly as possible. Air or other mixed gas is then allowed to flow along the tube in a slow stream, and collected as it issues. The gas or air which is, of course, reduced in volume, much gas penetrating through the clay tube into the air-pump vacuum, and the lighter gas the more rapidly, so that the proportion of the denser constituent in the gas collected. In one experiment, the proportion of oxygen in the air, after traversing the atmolyzer, was increased from 20.8 per cent, which is the normal proportion, to 24.5 per cent. With a mixture of oxygen and hydrogen, the separation is, of course, still more complete.

A distinction must be carefully drawn between real diffusion through membranes, and the apparently similar passage of gases through membranes, such as caoutchouc, bladder, gold-beaters' skin, etc. The mode of passage, which is called osmose, the rate of interchange being partly on the relative diffusibilities of the gases, partly on the degrees of adhesion exerted by the membrane on the different gases, in virtue of which the gas which adheres most powerfully penetrates the diaphragm most easily, and, attaining the opposite surface, passes to the other. A sheet of caoutchouc tied over the mouth of a wide-bottle filled with hydrogen, is soon pressed inwards, even to burst; the bottle be filled with air, and placed in an atmosphere of hydrogen, swelling and bursting take place outwards. If the membrane is in contact with a liquid, the result is likewise affected by the different solubilities of the gases in the water or other liquid which wets it. For example, the diffusive power of carbonic acid into atmospheric air is very small, but it passes rather through a wet bladder with the utmost ease, in virtue of its solubility in the water with which the membrane is moistened. It is by means of this process that the function of respiration is performed: the aëration of the blood in the lungs, and the disengagement of the carbonic acid, are effected through wet membranes; the blood is never brought into actual contact with the air, but receives its supply of oxygen, and disengages carbonic acid, by this kind of spurious diffusion.

The high diffusive power of hydrogen against air renders it impossible to keep that gas for any length of time in a bladder or caoutchouc bag; it is unsafe to keep it long in a gas-holder, lest it should become mixed with air by slight accidental leakage, and rendered explosive.

The passage of gases through membranes like caoutchouc or varnished paper, as well as through wet membranes like bladder, appears to depend on the actual liquefaction of the gases, which then become capable of passing through the substance of the membrane (as ether and naphtha do), and again evaporate on the surface and appear as gases. The unabsorption of gases in this manner often effects a much more complete separation of the components of a gaseous mixture than can be attained by the atmolytic method above described. Thus, Graham has found that oxygen is absorbed and condensed by caoutchouc two-and-a-half times more abundantly than nitrogen, and that when one side of a thin film is freely exposed to the air, while a vacuum is produced on the other side, the film allows 41.6 per cent. of oxygen to pass through, of the 21 per cent. usually present in the air, so that the air which has passed through is capable of rekindling wood burning without flame.

Metals appear to possess this power of absorbing and liquefying gases. Davy and Troost have observed the remarkable fact that hydrogen is capable of penetrating platinum and iron tubes, at a red heat, and that it is of opinion that this effect may be connected with a power

resistent in these and certain other metals to absorb and liquefy hydrogen, possibly in its character as a metallic vapor. Platinum in the form of wire or plate, at a low red heat, can take up 3.8 volumes of hydrogen measured cold, and palladium foil condenses as much as 643 times its volume of hydrogen at a temperature below 100°C . In the form of sponge, platinum absorbed 1.48 times its volume of hydrogen, and palladium 90 volumes. This absorption of gases by metals is called *occlusion*.*

The meteoric iron of Lenarto contains a considerable quantity of occluded hydrogen. When placed in a good vacuum, it yields 2.85 times its volume of gas, of which 85.68 per cent. consist of hydrogen, with 4.46 carbon monoxide and 9.86 nitrogen. Now, hydrogen has been recognized by spectrum analysis in the light of the fixed stars, and constitutes, according to the observations of Father Secchi, the principal element in the atmosphere of a numerous class of stars. "The iron of Lenarto," says Mr. Graham, "has, no doubt, come from such an atmosphere, in which hydrogen greatly prevailed. This meteorite may be looked upon as holding imprisoned within it, and bringing to us, the hydrogen of the stars."†

The rates of effusion of gases, that is to say, their rates of passage through a minute aperture in a thin plate of metal or other substance into a vacuum, follow the same law as their rates of diffusion, that is to say, they are inversely as the square roots of the densities of the gases. Nevertheless, the phenomena of diffusion and effusion are essentially different in their nature, the effusive movement affecting masses of a gas, whereas the diffusive movement affects only molecules; and a gas is usually carried by the former kind of impulse with a velocity many thousand times greater than by the latter. Mixed gases are effused at the same rates as one gas of the actual density of the mixture: and no separation of the gases occurs, as in *diffusion* into a vacuum.

The law of effusion just stated is true only under the condition that the gas shall pass through a minute aperture in a very thin plate. If the plate be thicker, so that the aperture becomes a tube, very different rates of efflux are observed; and when the capillary tube becomes considerably elongated, so that its length exceeds its diameter at least 400 times, the rates of flow of different gases into a vacuum again assume a constant ratio to each other, following, however, a law totally distinct from that of effusion. The principal general results observed with relation to this phenomenon of "Capillary Transpiration" are as follows:—

1. The rate of transpiration of the same gas increases, *ceteris paribus*, directly as the pressure: in other words, equal volumes of gas at different densities require times inversely proportional to their densities.
2. With tubes of equal diameter, the volume transpired in equal times is inversely as the length of the tube.
3. As the temperature rises, the transpiration of equal volumes becomes slower.
4. The rates of transpiration of different gases bear a constant relation to each other, totally independent of their densities, or, indeed, of any known property of the gases. Equal *weights* of oxygen, nitrogen, and carbon monoxide are transpired in equal times; so likewise are equal weights of nitrogen, nitrogen dioxide, and carbon monoxide; and of hydrogen chloride, carbon dioxide, and nitrogen monoxide‡.

* Graham, Phil. Trans. 1866; Journal of the Chemical Society [2], v. 236.

† Proceedings of the Royal Society, xv. 602.

‡ Graham, Phil. Trans. 1847, p. 691, and 1849, p. 340; also Elements of Chemistry, 2d ed. 1. 82.

COMBINATION OF HYDROGEN WITH OXYGEN.

It has been already stated, that although the light emitted by the flame of pure hydrogen is exceedingly feeble, yet the temperature of the flame is very high. The temperature may be still further exalted by previously mixing the hydrogen with as much oxygen as it requires for combination, that is, as will presently be seen, with half its volume. Such a mixture burns, like gunpowder, independently of the external air. When raised to the temperature required for combination, the two gases unite with explosive violence. If a strong bottle, holding not more than half a pint, be filled with such a mixture, the introduction of a lighted match or red-hot wire determines in a moment the union of the gases. By certain precautions, a mixture of oxygen and hydrogen can be burned at a jet without communication of fire to the contents of the vessel; the flame is in this case *solid*.

A little consideration will show, that all ordinary flames burning in the air or in pure oxygen are, of necessity, hollow. The act of combustion is nothing more than the energetic union of the substance burned with the surrounding oxygen; and this union can take place only at the surface of the burning body. Such is not the case, however, with the flame now under consideration; the combustible and the oxygen are already mixed, and only require to have their temperature a little raised to cause them to combine in every part. The flame so produced is very different in physical characters from that of a simple jet of hydrogen or any other combustible gas; it is long and pointed, and very remarkable in appearance.

Hanning's safety-jet, the construction of which involves a principle not yet discussed, may be adapted to a common bladder containing the mixture, and held under the arm, and the gas forced through the jet by a little pressure. Although this jet, properly constructed, is believed to be safe, it is best to use nothing stronger than a bladder, for fear of injury in the event of an explosion. The gases are often contained in separate reservoirs, a pair of large gas-holders, for example, and only suffered to mix in the jet itself, as in the contrivance of the late Professor Daniell; in this way all danger is avoided. The eye speedily becomes accustomed to the peculiar appearance of the true oxyhydrogen flame, so as to permit the supply of each gas to be exactly regulated by suitable stopcocks attached to the jet (fig. 89).

A piece of thick platinum wire introduced into the flame of the oxyhydrogen blowpipe melts with the greatest ease; a watch-spring or a small steel file burns with the utmost brilliancy, throwing off showers of beautiful sparks; an incombustible oxidized body, as magnesia or lime, becomes so intensely ignited as to glow with a light insupportable to the eye, and to be susceptible of employment as a most powerful illuminator, as a substitute for the sun's rays in the solar microscope, and for night signals in trigonometrical surveys.

If a long glass tube, open at both ends, be held over a jet of hydrogen (fig. 90) a series of musical sounds is sometimes produced by the partial extinction and rekindling of the flame by the ascending current of air. These little explosions succeed each other at regular intervals, and so rapidly as to give rise to a musical note, the pitch depending chiefly upon the length and diameter of the tube.

Although oxygen and hydrogen may be kept mixed at common temperatures for any length of time without combination taking place, yet, under particular circumstances, they unite quietly and without explosion. Many years ago, Döbereiner made the curious observation, that finely divided platinum possessed the power of determining the union of the gases; and, more recently, Faraday has shown that the state of minute division is by

no means indispensable, since rolled plates of the metal have the same property, provided their surfaces are absolutely clean. Neither is the effect strictly confined to platinum; other metals, as palladium and gold, and even stones and glass, exhibit the same property, although to a far

Fig. 89.



Fig. 90.



inferior degree, since they often require to be aided by a little heat. When a piece of platinum foil, which has been cleaned by hot oil of vitriol and thorough washing with distilled water, is thrust into a jar containing a mixture of oxygen and hydrogen standing over water, combination of the two gases immediately begins, and the level of the water rapidly rises, whilst the platinum becomes so hot that drops of water accidentally falling upon it enter into ebullition. If the metal be very thin and exceedingly clean, and the gases very pure, its temperature rises after a time to actual redness, and the residue of the mixture explodes. But this is an effect altogether accidental, and dependent upon the high temperature of the platinum, which high temperature has been produced by the preceding quiet combination of the two bodies. When the platinum is reduced to a state of minute division, and its surface thereby much extended, it becomes immediately red-hot in a mixture of hydrogen and oxygen, or hydrogen and air; a jet of hydrogen thrown upon a little of the spongy metal, contained in a glass or capsule, is at once kindled, and on this principle machines for the production of instantaneous light have been constructed. These, however, act well only when constantly used; the spongy platinum is apt to become damp by absorption of moisture from the air, and its power is then for the time lost.

The best explanation that can be given of these curious effects is to suppose that solid bodies in general have, to a greater or less extent, the property of condensing gases upon their surfaces, or even liquefying them (as shown, p. 133), and that this faculty is exhibited pre-eminently by certain of the non-oxidizable metals, as platinum and gold. Oxygen and hydrogen may thus, under these circumstances, be brought, as it were, *within the sphere of their mutual attractions* by a temporary increase of density, whereupon combination ensues.

Coal-gas and ether or alcohol vapor may be made to exhibit the phenomenon

quiet oxidation under the influence of this remarkable surface-action. A spiral of slender platinum wire, a roll of thin foil, or even a common platinum crucible, heated to dull redness, and then held in a jet of mixed gas, becomes strongly ignited, and remains in that state as long as the supply of mixed gas and air is kept up, the temperature being maintained by the heat disengaged in the act of union. Sometimes the metal becomes white-hot, and then the gas takes fire.

If such a coil of wire be attached to a card, and suspended in a glass containing a few drops of ether, having previously been made red-hot in the flame of a spirit-lamp, it will continue to glow until the oxygen of the air is exhausted, giving rise to the production of an irritating vapor which attacks the eyes. The combustion of the ether is in this case but partial: a portion of its hydrogen is alone removed, and the whole of the carbon left untouched.

A coil of thin platinum wire may be placed over the wick of a spirit-lamp, or a ball of spongy platinum sustained just above the cotton; on lighting the lamp, and then blowing it out as soon as the metal appears red-hot, slow combustion of the spirit drawn up by the capillarity of the wick will take place, accompanied by the pungent vapors just mentioned, which may be modified, and even rendered agreeable, by dissolving in the liquid some sweet-smelling essential oil or resin.

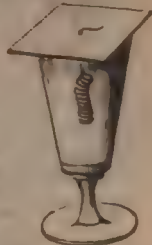
Hydrogen forms numerous compounds with other bodies, although it is greatly surpassed in this respect not only by oxygen, but by many of the other elements. In many of its chemical relations it resembles the metals, combining with oxygen, sulphur, chlorine, bromine, etc., to form compounds analogous in constitution to the metallic oxides, sulphides, chlorides, bromides, etc. (p. 127).

Oxides of Hydrogen.—There are two oxides of hydrogen—namely, the monoxide, which is water, and the dioxide, discovered in the year 1818 by Thénard.

It appears that the composition of water was first demonstrated in the year 1781 by Cavendish;* but the discovery of the exact proportions in which oxygen and hydrogen unite in generating that most important compound has, from time to time to the present day, occupied the attention of some of the most distinguished cultivators of chemical science. There are two distinct methods of research in chemistry—the *analytical*, or that in which the compound is resolved into its elements, and the *synthetical*, in which the elements are made to unite and produce the compound. The first method is of much more general application than the second; but in this particular instance both may be employed, although the results of the synthesis are the more valuable.

The decomposition of water may be effected by voltaic electricity. When water is acidulated so as to render it a conductor,† and a portion interposed between a pair of platinum plates connected with the extremities of a voltaic apparatus of moderate power, decomposition of the liquid takes place in a very interesting manner; oxygen, in a state of perfect purity, is evolved from the water in contact with the plate belonging to the copper

Fig. 91.



* A claim to the discovery of the composition of water, on behalf of James Watt has been very strongly urged, and supported by such evidence that the reader of the controversy may be led to the conclusion that the discovery was made by both parties, nearly simultaneously, and unknown to each other. See the article "Gase," by Dr. Paul, in Watt's Dictionary of Chemistry, II. 789.

† See the section on "Electro-Chemical Decomposition."

Fig. 92.



end of the battery, and hydrogen, equally pure, is disengaged at the plate connected with the zinc extremity, the middle portions of liquid remaining apparently unaltered. By placing small graduated jars over the platinum plates, the gases can be collected, and their quantities determined. The whole arrangement is shown in fig. 92; the conducting wires pass through the bottom of the glass cup, and away to the battery.

When this experiment has been continued a sufficient time, it will be found that the volume of the hydrogen is a very little above twice that of the oxygen. Were it not for the accidental circumstance of oxygen being sensibly more soluble in water than hydrogen, the proportion of two to one by measure would come out exactly.

Water, as Mr. Grove has shown, is likewise decomposed into its constituents by heat. This effect is produced by introducing platinum balls, ignited by electricity or other means, into water or steam. The two gases are obtained in very small quantities at a time.

When oxygen and hydrogen, both as pure as possible, are mixed in the

Fig. 93.



proportions mentioned, passed into a strong glass tube standing over mercury, and exploded by the electric spark, all the mixture disappears, and the mercury is forced up into the tube, filling it completely. The same experiment may be made with the explosion vessel or audiometer of Cavendish (fig. 93). The instrument is exhausted at the air-pump, and then filled from a cappel jar with the mixed gases; on passing an electric spark by the wires shown at *a*, explosion ensues, and the glass becomes bedewed with moisture; and if the stopcock be then opened under water, the latter will rush in and fill the vessel, leaving merely a bubble of air, the result of imperfect exhaustion.

The process upon which most reliance is placed is that in which pure copper oxide is reduced at a red heat by hydrogen, and the water so formed is collected and weighed. This oxide suffers no change by heat alone, but the momentary contact of hydrogen, or any common combustible matter, at a high temperature, suffices to reduce a corresponding portion to the metallic state. Fig. 94 will serve to convey some idea of the arrangement adopted in researches of this kind.



A copious supply of hydrogen is procured by the action of dilute sulphuric acid upon the purest zinc that can be obtained; the gas is made to pass in succession through solutions of silver nitrate and strong caustic potash, by which its purification is completed. After this it is conducted through a tube three or four inches long, filled with fragments of pumice stone steeped in concentrated oil of vitriol, or with anhydrous phosphoric acid. These substances have so great an attraction for aqueous vapors, that they dry the gas completely during its transit. The extremity of this tube is shown at *a*. The dry hydrogen thus arrives at the part of the apparatus containing the copper oxide represented at *b*; this consists of a two-necked flask of very hard white glass, maintained at a red heat by a spirit lamp placed beneath. As the decomposition proceeds, the water produced by the reduction of the oxide

begins to condense in the second neck of the flask, whence it drops into receiver c. A second desiccating tube prevents the loss of aqueous vapor by the current of gas which passes in excess.

Fig. 94.



Before the experiment can be commenced, the copper oxide, the purity of which is well ascertained, must be heated to redness for some time in a current of dry air; it is then suffered to cool, and very carefully weighed with the flask. The empty receiver and second drying-tube are also weighed, the disengagement of gas set up, and when the air has been displaced heat is slowly applied to the oxide. The action is at first very energetic, the oxide often exhibits the appearance of ignition; but as the decomposition proceeds, it becomes more sluggish, and requires the application of a considerable heat to effect its completion.

When the process is at an end, and the apparatus perfectly cool, the stream of gas is discontinued, dry air is drawn through the whole arrangement, and, lastly, the parts are disconnected and reweighed. The loss of the copper oxide gives the oxygen; the gain of the receiver and its drying-tube indicates the water; and the difference between the two, the hydrogen.

A set of experiments, made in Paris in the year 1820, by Dulong and Berzelius, gave as a mean result, for the composition of water by weight, 8 parts oxygen to 1 part hydrogen; numbers so nearly in the proportion of 8 to 1, that the latter have usually been assumed to be true.

More recently the subject has been reinvestigated by Dumas, with the most scrupulous precision, and the above supposition fully confirmed. The composition of water may therefore be considered as established; it contains by weight 8 parts oxygen to 1 part hydrogen, and by measure, 1 volume oxygen to 2 volumes hydrogen. The densities of the gases, as already mentioned, correspond very closely with these results.

The physical properties of water are too well known to need lengthened description: when pure, it is colorless and transparent, destitute of taste and odor, and an exceedingly bad conductor of electricity of low tension. It attains its greatest density towards 4.5°C . (40°F .), freezes at 0°C . (32°F .),* and boils under the ordinary atmospheric pressure at or near 100°C . (212°F .). It evaporates at all temperatures.

The weight of a cubic centimetre of water at the maximum density is chosen as the unit of weight of the metrical system; and called a gram; consequently a litre or cubic decimetre = 100 cubic centimetres of water, at the same temperature, weighs 1000 grams, or 1 kilogram.

A cubic inch of water at 62°F . weighs 252.45 grains; a cubic foot weighs nearly 1000 ounces avoirdupois; and an imperial gallon weighs 70,000 grains, or 10 lbs. avoirdupois.

Water is 825 times heavier than air. To all ordinary observation, it is incompressible; very accurate experiments have nevertheless shown that it does yield to a small extent when the power employed is very great,

* According to Dufour, the specific gravity of ice is 0.9175; water, therefore, on freezing, expands by $\frac{1}{11}$ of its volume.

the diminution of volume for each atmosphere of pressure being about 51-millionths of the whole.

Clear water, although colorless in small bulk, is blue like the atmosphere when viewed in mass. This is seen in the deep ultramarine tint of the ocean, and perhaps in a still more beautiful manner in the lakes of Switzerland and other Alpine countries, and in the rivers which issue from them, the slightest admixture of mud or suspended impurity destroying the effect. The same magnificent color is visible in the fissures and caverns found in the ice of the glaciers, which is usually extremely pure and transparent within, although foul upon the surface.

The specific gravity of steam or vapor of water is found by experiment to be 0.625, compared with air at the same temperature and pressure, or 9 as compared with hydrogen. Now, it has been already shown that water is composed of two volumes of hydrogen and one volume of oxygen; and if the weight of one volume of hydrogen be taken as unity, that of two volumes hydrogen ($=2$) and one volume oxygen ($=16$) will together make 18, which is the weight of two volumes of water-vapor. Consequently *water in the state of vapor consists of two volumes of hydrogen and one volume of oxygen condensed into two volumes.* A method of demonstrating this important fact by direct experiment has been devised by Dr. Hofmann. It consists in exploding a mixture of two volumes hydrogen and one volume oxygen, by the electric spark, in a eudiometer tube inclosed in an atmosphere of the vapor of a liquid (amylie alcohol) which boils at a temperature considerably above that of boiling water, so that the water produced by the combination of the gases remains in the state of vapor instead of at once condensing to the liquid form. It is then seen that the three volumes of mixed gas are reduced after the explosion to two volumes.*

Water seldom or never occurs in nature in a state of perfect purity: even the rain which falls in the open country contains a trace of ammoniacal salt, while rivers and springs are invariably contaminated to a greater or less extent with soluble matters, saline and organic. Simple filtration through a porous stone or a bed of sand will separate suspended impurities, but distillation alone will free the liquid from those which are dissolved. In the preparation of distilled water, which is an article of large consumption in the scientific laboratory, it is proper to reject the first portions which pass over, and to avoid carrying the distillation to dryness. The process may be conducted in a metal still furnished with a worm or condenser of silver or tin; lead must not be used.

The ocean is the great recipient of the saline matter carried down by the rivers which drain the land: hence the vast accumulation of salts. The following table will serve to convey an idea of the ordinary composition of sea-water; the analysis is by Dr. Schweitzer,† of Brighton, the water being that of the British Channel:—

| 1000 grains contained— | |
|---|----------|
| Water | 964.745 |
| Sodium chloride | 27.059 |
| Potassium chloride | 0.766 |
| Magnesium chloride | 3.666 |
| Magnesium bromide | 0.029 |
| Magnesium sulphate | 2.296 |
| Calcium sulphate | 1.406 |
| Calcium carbonate | 0.033 |
| Traces of Iodine and Ammoniacal salts | ... |
| | 1000.000 |

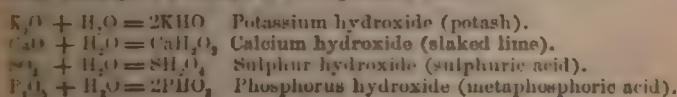
* For a description of the apparatus, see Hofmann's *Modern Chemistry* (1865), p. 61.

† *Philosophical Magazine*, July 1839.

Its specific gravity was found to be 1.0274 at 15.50° C. (60° F.). Sea-water is liable to variations of density and composition by the influence of local causes, such as the proximity of large rivers, or masses of melting ice, and other circumstances.

Natural springs are often impregnated to a great extent with soluble substances derived from the rocks they traverse; such are the various mineral waters scattered over the whole earth, and to which medicinal virtues are attributed. Some of these hold ferrous oxide in solution, and are effervescent from carbonic acid gas; others are alkaline, probably from traversing rocks of volcanic origin; some contain a very notable quantity of iodine or bromine. Their temperatures, also, are as variable as their chemical nature.

Water acts on many oxides, both acid and basic, with great energy and considerable evolution of heat, producing compounds called hydroxides, which contain hydrogen and oxygen in the proportion to form water, but not actually existing as water, the elements of the two bodies in combining having undergone a change of arrangement, thus:—



In many of these compounds the elements of water are retained with great force, and require a high temperature to expel them: calcium hydroxide, for example, requires a red heat to convert it into anhydrous calcium oxide (quick-lime), and the hydroxides of potassium, barium, sulphur, and phosphorus cannot be dehydrated by heat alone.

In other cases, water appears to combine with other bodies—salts, for example—as such, or, in other words, without alteration of atomic arrangement. Such compounds are called hydrates, and the water contained in them—the presence of which has great influence on the crystalline form of the compound—is called water of crystallization. Water thus combined is easily expelled by heat, mostly at 100–120° F.

Many salts combine with different quantities of water, according to the temperature at which they separate from solution, the quantity thus taken up being, for the most part, greater as the temperature of solidification is lower: thus, sodium carbonate crystallizes from solution at ordinary temperatures in oblique rhombic prisms containing 10 molecules of water ($\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$), whereas at higher temperatures it crystallizes as $\text{Na}_2\text{CO}_3 + 8\text{H}_2\text{O}$ or $5\text{H}_2\text{O}$, and from a boiling solution in rectangular plates containing $\text{CO}_3\text{Na}_2 + \text{H}_2\text{O}$.

There are also hydrates called cryohydrates,* which exist only at temperatures below the freezing point of water; thus, sodium chloride (common salt), which at ordinary temperatures crystallizes in anhydrous cubes, solidifies at -23°C . (-9.4°F .) with 10½ molecules of water, forming the hydrate $\text{NaCl} + 10\frac{1}{2}\text{H}_2\text{O}$, or $2\text{NaCl} + 21\text{H}_2\text{O}$, and ammonium chloride (sal-ammoniac), also anhydrous at ordinary temperatures, solidifies at -15°C . (-5°F .) to a hydrate containing $\text{NH}_4\text{Cl} + 12\text{H}_2\text{O}$.

In some cases, water of crystallization is so forcibly combined that it gradually separates when the substance containing it is exposed at ordinary temperatures to dry air, the salt at the same time losing its crystalline character and falling to powder. This change, called efflorescence, is strikingly exhibited by crystallized sodium carbonate and common alum. On the other hand, many substances which are very soluble in water attract water from moist air in such quantity as to form a solution, this

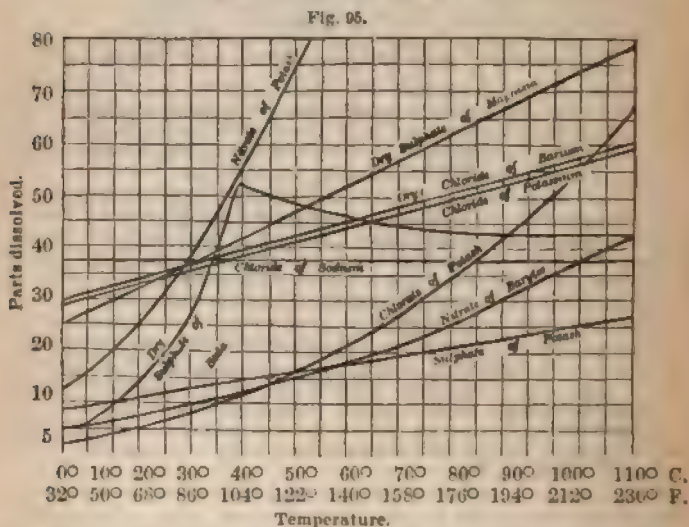
* Guthrie, *Phil. Mag. (Ser. 4) alt.*, 1, 203; 1, 26; —(‘cr.’) 1, 40; 11, 211.

change, which is exhibited by calcium chloride and potassium hydroxide (caustic potash), is called deliquescence.

Lastly, the solvent properties of water far exceed those of any other liquid known. Among salts a very large proportion are soluble to a greater or less extent, the solubility usually increasing with the temperature, so that a hot saturated solution deposits crystals on cooling. There are a few exceptions to this law, one of the most remarkable of which is common salt, the solubility of which is nearly the same at all temperatures: the hydroxide and certain organic salts of calcium, also, dissolve more freely in cold than in hot water.

Fig. 95 exhibits the unequal solubility of different salts in water of different temperatures. The lines of solubility cut the verticals raised from points indicating the temperatures, upon the lower horizontal line, at heights proportioned to the quantities of salt dissolved by 100 parts of water. The diagram shows, for example, that 100 parts of water dissolve of potassium sulphate 8 parts at 0°C ., 17 parts at 50° , and 25 parts at

Solubility of Salts in 100 parts of Water.



1000. There are salts which, like sodium chloride, possess, as already mentioned, very nearly the same degree of solubility in water at all temperatures; in others, like potassium sulphate or potassium chloride, the solubility increases directly with the increment of temperature; in others, again, like potassium nitrate or potassium chlorate, the solubility augments much more rapidly than the temperature. The differences in the deportment of these different salts are shown very conspicuously, by a straight horizontal line, by a straight inclined line, and lastly, by curves, the convexity of which is turned towards the lower horizontal line.

The solubility of a salt is usually represented by the quantity of anhydrous salt dissolved by 100 parts of water. It is obvious, however, that salts containing water of hydration or water of crystallization cannot, within

limits of temperature, dissolve in water in the anhydrous state, but be dissolved as hydrates. The solubility of a hydrated salt frequently differs very considerably from that of the same salt in the anhydrous state. Again, many salts, as already observed, form more than one hydrate, and these several hydrates may also differ in their solubility. Sodium sulphate forms a hydrate, $\text{SO}_4\text{Na}_2 + 7\text{H}_2\text{O}$, consisting, in 100 parts, of 47 parts of anhydrous salt and 47 parts of water, which is obtained in solution when a solution of sodium sulphate saturated at 100°C . is cooled in contact with the air: this hydrate is much more soluble than the anhydrous salt. Another hydrate $\text{SO}_4\text{Na}_2 + 10\text{H}_2\text{O}$ (Glauber's salt), which differs from the former in its crystalline form, and consists, in 100 parts, of 44.2 parts of anhydrous salt and 55.8 parts of water. When a solution of sodium sulphate is saturated at the boiling point of water, and cooled to the common temperature without depositing any crystals, the salt exists in the form of the more soluble hydrate. This salt, when coming in contact with the air, or with a small crystal of common Glauber's salt, is suddenly transformed into the less soluble hydrate, part of which separates from the solution in the form of Glauber's salt. From 0° to 33°C . (32°F .) sodium sulphate dissolves as Glauber's salt, the solubility of which increases with the temperature: hence the rapid rise of the curve indicating the solubility of the salt. Above 33°C . (91°F .) the hydrate of sodium sulphate is decomposed, even in solution, being more and more gradually converted into the anhydrous salt as the temperature increases. Anhydrous sulphate appears, however, far less soluble in the anhydrous state, hence the diminution of solubility of the salt when its solution is cooled above 33°C . (91°F .)

Diffusion. Dialysis.—When a solution having a sp. gr. greater than water is introduced into a cylindrical glass vessel, and then water is cautiously poured upon it, in such a manner that the two layers of liquid remain unmixed, the substance dissolved in the lower liquid will gradually pass into the supernatant water, though the vessel may have been left undisturbed, and the temperature remain unchanged. This gradual passage of a dissolved substance from its original solution into another liquid, taking place notwithstanding the higher specific gravity of the substance which opposes this passage, is called the *diffusion of liquids*. The phenomena of this diffusion have been elaborately investigated by Graham, who has arrived at very important results. Different substances, in solution of the same concentration, and under other similar circumstances, diffuse with very unequal velocity. Hydrochloric acid, for example, diffuses with greater rapidity than potassium chloride, potassium chloride more rapidly than sodium chloride, and the latter, again, more rapidly than magnesium sulphate; gelatin, albumen, and caramel diffuse very slowly. Diffusion is generally found to take place more rapidly at higher than at low temperatures. Diffusion is more particularly rapid with gaseous substances, though not exclusively, for hydrochloric acid and ammonia are among the highly diffusive bodies. Diffusion is slow with non-gaseous bodies, which, like gelatin, are capable of forming a jelly, though even here exceptions are met with. Graham calls the substances of high diffusibility *crystalloids*, the substances of low diffusibility *colloids*. The unequal power of diffusion with which different substances are endowed frequently furnishes the means of separating them. When water is added with caution, so as to prevent mixing, upon a solution containing equal quantities of potassium chloride and sodium chloride, the more soluble potassium chloride travels more rapidly upwards than the less soluble sodium chloride, and very considerable portions of potassium chloride will have reached the upper layers of the water before the sodium

chloride has arrived there in appreciable quantity. The separation of rapidly diffusible crystalloids and slowly diffusible colloids succeeds still better.

A more perfect separation of crystalloids and colloids may be accomplished in the following manner: Graham made the important observation, that certain membranes, and also parchment paper, when in contact, on the one surface, with a solution containing a mixture of crystalloidal and colloidal substances, and, on the other surface, with pure water, will permit the passage to the water of the crystalloids, but not of the colloids. To carry out this important mode of separation, which is designated by the term *dialysis*, the lower mouth of a glass vessel, open at top and bottom (fig. 96), is tied over with parchment paper, placed upon an appropriate support (fig. 97), and transferred, together with the latter, into a larger vessel filled with water (fig. 99); or the vessel may be suspended, as shown in fig. 98. The liquid containing the different substances in solution is then poured into the inner vessel, so as to form a layer of about

Fig. 96.



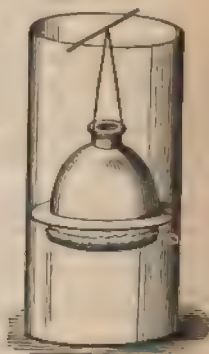
Fig. 97.



Fig. 99.



Fig. 98.



half an inch in height upon the parchment paper. The crystalloidal substances gradually pass through the parchment paper into the outer water, which may be renewed from time to time; the colloidal substances are almost entirely retained by the liquid in the inner vessel. In this manner Graham prepared several colloids free from crystalloids; he showed, moreover, that poisonous crystalloids, such as arsenious acid or strychnine, even when mixed with very large proportions of colloidal substances, pass over into the water of the dialyzer in such a state of purity that their presence may be established by re-agents with the utmost facility.

Osmose.—When two different liquids are separated by a porous diaphragm, as, for instance, by a membrane, and the liquids mix through this diaphragm, it is found that in most cases the quantities travelling in opposite directions are unequal. Suppose three cylinders, the lower mouths of which are tied over with bladders, filled respectively with concentrated solutions of copper sulphate, sodium chloride, and alcohol, and let them be immersed in vessels containing water, to such a depth that the liquids inside and outside are level (fig. 100). After some time the liquid within the tube is found to have risen appreciably above the level of the water (fig. 101). On the other hand, if the cylinder filled with pure water be immersed in a solution of copper sulphate, or of sodium

chloride, or in alcohol, the liquid in the cylinder is seen to diminish after some time (fig. 102). A larger quantity of water passes through the bladder into the solution of copper sulphate, of sodium chloride, or into alcohol, than the amount of either of these three liquids which passes

Fig. 100.

Fig. 101.

Fig. 102.



through the bladder into the water. The mixing of dissimilar substances through a porous diaphragm is called *osmose*. The passage in larger proportions of one liquid into another is designated by the term *exosmose*.

These phenomena are due to the attraction which the two liquids have for each other, and to the difference of the attraction exercised by the diaphragm upon these liquids. Bladder takes up a much larger quantity of water than of a solution of salt or of alcohol. Very rarely only one of the liquids traverses the diaphragm; generally two currents of unequal strength move in opposite directions. When water is separated by an animal membrane from a solution of salt or from alcohol, not only is a transition of water to these liquids observed, but a small quantity of hydrochloric acid and of alcohol also passes over into the water. In some cases, however, when colloidal substances in concentrated solutions are on one side of the diaphragm and water on the other, the latter alone traverses the diaphragm, not a trace of the former passing through to the water.

Water likewise dissolves gases. Solution of gases in water (or in other liquids) is called *absorption*, unless this solution gives rise to the formation of chemical compounds in definite proportions. The phenomena of absorption have been more particularly studied by Bunsen, to whom we are indebted for the most accurate examination of this subject.

Water dissolves very unequal quantities of the different gases, and very unequal quantities of the same gas at different temperatures. 1 vol. of water absorbs, at the temperatures stated in the table, and under the pressure of 30 inches of mercury, the following volumes of different gases, measured at 0° C. and 30 inches pressure:—

| | Oxygen. | Nitrogen. | Hydrogen. | Nitrogen monoxide. | Carbon dioxide. |
|-------|--------------------|-------------------------------|---------------------|--------------------|-----------------|
| 0° C. | 0.041 | 0.020 | 0.019 | 1.31 | 1.80 |
| 10° | 0.033 | 0.016 | 0.019 | 0.92 | 1.18 |
| 20° | 0.028 | 0.014 | 0.019 | 0.67 | 0.90 |
| | Hydrogen chloride. | Hydrogen sulphurous sulphide. | Hydrochloric oxide. | Hydrochloric acid. | Ammonia. |
| 0° C. | — | 4.37 | 53.9 | 505 | 1180 |
| 10° | 2.59 | 3.59 | 36.4 | 472 | 898 |
| 20° | 2.16 | 2.91 | 27.3 | 441 | 680 |
| 30° | 1.75 | 2.33 | 20.4 | 412 | 536 |
| 40° | 1.37 | 1.86 | 15.6 | 387 | 444 |

When the pressure increases, a larger quantity of the gases is absorbed. Gases moderately soluble in water follow in their solubility the law of Henry and Dalton, according to which the quantity of gas dissolved is proportional to the pressure. At 10°C . 1 vol. of water absorbs, under a pressure of 1 atmosphere, 1.18 vol. of carbon dioxide, measured at 0° and under a pressure of 30 inches mercury. The quantity of carbon dioxide dissolved under a pressure of 2 atmospheres, and measured under conditions precisely similar to those of the previous experiments, equals 2.36 vols. Again, 1 vol. of water dissolves under a pressure of $\frac{1}{2}$ atmosphere, 0.59 vol. of carbon dioxide also measured at 0° and under 30 inches of mercury. Gases which are exceedingly soluble in water do not obey this law, except at high temperatures, when the solubility has been already considerably diminished.

It deserves, however, to be noticed, that the pressure which determines the rate of absorption of a gas is by no means the general pressure to which the absorbing liquid is exposed, but that pressure which the gas under consideration would exert if it were alone present in the space with which the absorbing liquid is in contact. Thus, supposing water to be in contact with a mixture of 1 vol. of carbon dioxide and 3 vols. of nitrogen, under a pressure of 4 atmospheres, the amount of carbon dioxide dissolved by the water will be by no means equal to that which the water would have absorbed if it had been, at the same pressure of 4 atmospheres, in contact with pure carbon dioxide. In a mixture of carbon dioxide and nitrogen in the stated proportions, the carbon dioxide exercises only $\frac{1}{4}$, the nitrogen only $\frac{3}{4}$, of the total pressure of the gaseous mixture (4 atmospheres); the partial pressure due to the carbon dioxide is in this case 1 atmosphere, that due to the nitrogen 3 atmospheres; and water, though exposed to a pressure of 4 atmospheres, cannot, under these circumstances, absorb more carbon dioxide than it would if it were in contact with pure carbon dioxide under a pressure of 1 atmosphere.

It is necessary to bear this in mind in order to understand why the air which is absorbed by water out of the atmosphere differs in composition from atmospheric air. The latter consists very nearly of 21 vols. of oxygen and 79 vols. of nitrogen. In atmospheric air which acts under a pressure of 1 atmosphere, the oxygen exerts a partial pressure of $\frac{21}{100}$, the nitrogen a partial pressure of $\frac{79}{100}$ atmosphere. At 10°C . 1 vol. of water (see the above table) absorbs 0.033 vol. of oxygen and 0.016 vol. of nitrogen, supposing these gases to act in the pure state under a pressure of 1 atmosphere. But under the partial pressures just indicated, water at 10°C . cannot absorb more than $\frac{21}{100} \times 0.033 = 0.007$ of oxygen, and $\frac{79}{100} \times 0.016 = 0.13$ vol. of nitrogen. In $0.007 + 0.13 = 0.020$ vol. of the gaseous mixture absorbed by water, there are consequently 0.007 vol. of oxygen and 0.013 vol. of nitrogen, or in 20 vols. of this mixture, 7 vols. of oxygen and 13 vols. of nitrogen, or in 100 vols. of the gaseous mixture, 35 vols. of oxygen and 65 vols. of nitrogen. The air contained at the common temperature in water is thus seen to be very much richer in oxygen than ordinary atmospheric air. This property of water to absorb oxygen from the air more readily than nitrogen has been applied to the preparation of oxygen for industrial use.*

Air is pressed into water by means of a forcing-pump, and the gases which escape on diminishing the pressure are subjected to the same treatment eight times in succession, by which time nearly pure oxygen is obtained. The following table shows the composition of the gaseous mixture at each successive stage.—

* Mallet, Dingler's Polyt. Journal, excta. 112.

| Atmospheric
air. | Composition after successive pressures. | | | | | | | |
|---------------------|---|------|------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| . . . 79 | 66.67 | 52.5 | 37.5 | 25.0 | 15.0 | 9.0 | 5.0 | 2.7 |
| . . . 21 | 33.33 | 47.5 | 62.5 | 75.0 | 85.0 | 91.0 | 95.0 | 97.3 |

Water containing a gas in solution, when exposed in a vacuum or in a space filled with another gas, allows the gas absorbed to escape until the quantity retained corresponds with the share of the pressure belonging to the gas evolved. If the latter be constantly removed by a powerful absorbent or by a good air-pump, it is in most cases easy to separate every trace of gas from the water. The same result is obtained when water containing a gas in solution is exposed in a space of comparatively infinite space filled with another gas. Water in which nitrogen monoxide is dissolved loses the latter entirely by mere exposure to the atmosphere, and the gas evolved cannot, at any moment, exert more than an infinitely small share of the pressure. If water be freed from gases by ebullition, the separation depends partly upon the diminution of the solubility by the increase of temperature, partly also upon the formation above the surface of the liquid of a constantly renewed atmosphere into which the gas still retained by the liquid may escape.

Some gases which are absorbed in large quantities, and very quickly by water—hydrochloric acid, for instance—cannot be perfectly expelled either by the protracted action of another gas (exposure to the atmosphere) or by ebullition; in such cases the liquid, still charged with gas, evaporates as a whole when it has assumed a certain composition. This composition varies, however, with the temperature if the liquid be submitted to a current of air, and with the pressure if it be boiled.

Liquids also lose the gas they contain in solution by freezing: hence the air-bubbles in ice, which consist of the air which had been absorbed from the atmosphere by the water. Gas is retained by liquids at the freezing temperature only when it forms a chemical combination in definite proportion with the liquid. Water containing chlorine or sulphurous acid in solution freezes without evolution of gas, with formation of a solid hydrate of chlorine or sulphurous acid.

Pure water generally dissolves gases more copiously than water containing solid bodies in solution (salt water, for instance). If in some few cases exceptions are observed to take place, they appear to depend upon the formation of feeble but true chemical compounds in definite proportion; the fact that carbon dioxide is more copiously absorbed by water containing sodium phosphate in solution than by pure water, may perhaps be explained in this manner.

When water is heated in a strong vessel to a temperature above that of the ordinary boiling point, its solvent powers are still further increased. Mr. Turner inclosed in the upper part of a high-pressure steam-boiler, worked at 149° C. (300° F.), pieces of plate and crown glass. At the expiration of four months the glass was found completely corroded by the action of the water; what remained was a white mass of silica, destitute of alkali, while stalactites of siliceous matter, above an inch in length, depended from the little wire cage which inclosed the glass. This experiment tends to illustrate the changes which may be produced by the action of water at a high temperature in the interior of the earth upon felspathic and other rocks. The phenomenon is manifest in the Geyser springs of Iceland, which deposit *siliceous sinter*.

Hydrogen Dioxide, H_2O_2 , sometimes called *Oxygenated water*, is an exceedingly interesting substance, but very difficult of preparation. It is formed by dissolving barium dioxide in dilute hydrochloric acid carefully cooled by ice, and then precipitating the barium by sulphuric acid; the excess of oxygen of the dioxide, instead of being disengaged as gas, unites with a portion of the water, and converts it into hydrogen dioxide. This treatment is repeated with the same solution and fresh portions of the barium dioxide, until a considerable quantity of the latter has been consumed, and a corresponding amount of the hydrogen dioxide formed. The liquid yet contains hydrochloric acid, to get rid of which it is treated in succession with silver sulphate and baryta water. The whole process requires the utmost care and attention. The barium dioxide itself is prepared by exposing pure baryta, contained in a red-hot porcelain tube, to a stream of oxygen. The solution of hydrogen dioxide may be concentrated under the air-pump receiver until it acquires the specific gravity of 1.45. In this state it presents the aspect of a colorless, transparent, inodorous liquid, possessing remarkable bleaching powers. It is very prone to decomposition; the least elevation of temperature causes effervescence, due to the escape of oxygen gas; near $100^{\circ}C$. it is decomposed with explosive violence. Hydrogen dioxide contains exactly twice as much oxygen as water, or 16 parts to one part of hydrogen.

NITROGEN.

Atomic weight, 14; symbol, N.

NITROGEN* constitutes about four-fifths of the atmosphere, and enters into a great variety of combinations. It may be prepared by several methods. One of the simplest of these is to burn out the oxygen from a confined portion of air by phosphorus, or by a jet of hydrogen.

A small porcelain capsule is floated on the water of the pneumatic trough, and a piece of phosphorus is placed in it and set on fire. A bell-jar is then inverted over the whole, and suffered to rest on the shelf of the trough, so as to project a little over its edge. At first the heat causes expansion of the air of the jar, and a few bubbles are expelled, after which the level of the water rises considerably. When the phosphorus becomes extinguished by exhaustion of the oxygen, and time has been given for the subsidence of the cloud of finely divided snow-like phosphoric oxide which floats in the residual gas, the nitrogen may be transferred into another vessel, and its properties examined.



Fig. 103.

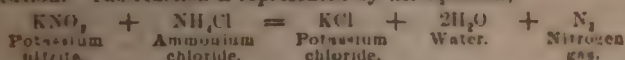
Prepared by the foregoing process, nitrogen is contaminated with a little vapor of phosphorus, which communicates its peculiar odor. A preferable method is to fill a porcelain tube with turnings of copper, or, still better, with the spongy metal obtained by reducing the oxide with hydrogen; to heat this tube to redness; and then pass through it a slow stream of atmospheric air, the oxygen of which is entirely removed, during its progress, by the heated copper.

If chlorine gas be passed into solution of ammonia, the latter substance, which is a compound of nitrogen with hydrogen, is decomposed; the chlorine combines with the hydrogen, and the nitrogen is set free, with effervescence.

* *i. e.*, Generator of nitre; also called Azote, from *a*, privative, and *zen*, life.

resence. In this manner very pure nitrogen can be obtained. In making this experiment, it is necessary to stop short of saturating or decomposing the whole of the ammonia; otherwise there will be great risk of accident from the formation of an exceedingly dangerous explosive compound, produced by the contact of chlorine with an ammoniacal salt.

Another very easy and perfectly safe method of obtaining pure nitrogen is to decompose a solution of potassium nitrite with ammonium chloride (sal-ammoniac). The potassium nitrite is prepared by passing the red vapors of nitrous acid, obtained by heating dilute nitric acid with starch, into a solution of caustic potash. On boiling the resulting solution with sal-ammoniac, nitrogen gas is evolved, while potassium chloride remains in solution. The reaction is represented by the equation,



Nitrogen is destitute of color, taste, and odor; it is a little lighter than air, its density being 0.972. A litre of the gas at 0° C. and 760 mm. barometrical pressure weighs 1.25658 gram. 100 cubic inches, at 15.5° C. (60° F., and 30 inches barometer, weigh 30.14 grams. Nitrogen is incapable of sustaining combustion of animal life, although, like hydrogen, it has no positive poisonous properties; neither is it soluble to any notable extent in water or caustic alkali; it is, in fact, best characterized by negative properties.*

Atmospheric Air.—The exact composition of the atmosphere has repeatedly been made the subject of experimental research. Besides nitrogen and oxygen, the air contains a little carbon dioxide (carbonic acid), a very variable proportion of aqueous vapor, a trace of ammonia, and, perhaps, a little carburetted hydrogen. The oxygen and nitrogen are in a state of mixture, not of combination, yet their ratio is always uniform. Air has been brought from lofty Alpine heights, and compared with that from the plains of Egypt; it has been brought from an elevation of 21,000 feet by the aid of a balloon; it has been collected and examined in London and Paris, and many other places; still, the proportion of oxygen and nitrogen remains unaltered, the diffusive energy of the gases being adequate to maintain this perfect uniformity of mixture. The carbon dioxide, on the contrary, being much influenced by local causes, varies considerably. In the following table the proportions of oxygen and nitrogen are given on the authority of Dumas, and the carbon dioxide on that of De Saussure: the ammonia, the discovery of which in atmospheric air is due to Liebig, is too small in quantity for direct estimation.

Composition of the Atmosphere.

| | By weight. | By measure. |
|--------------------|------------|-------------|
| Nitrogen | 77 parts. | 79.19 |
| Oxygen | 23 " | 20.81 |
| | 100 | 100.00 |

Carbon dioxide, from 3.7 measures to 6.2 measures in 10,000 measures of air. Aqueous vapor variable, depending much upon the temperature. Ammonia, a trace.

* On the receipt by the French Academy of the Intelligence of the liquefaction of oxygen by M. Pictet (p. 123), it was announced that M. Cailletet had obtained the same result, and not only with oxygen but also with carbon monoxide, nitrogen dioxide, nitrogen, and hydrogen. Nitrogen became visible on exit from a jet pipe (pressure 260 at.) as little drops, but hydrogen (260 at.) only as a vapoury cloud,—a success not equal to the condensation of carbon dioxide or nitrogen monoxide.—R. H.

Dr. Frankland has analyzed samples of air taken by himself in the valley of Chamouni, on the summit of Mont Blanc, and at the Grands Mulets. The following are the results of his analyses:—

| | Carbon Dioxide. | Oxygen. |
|---------------------------------|-----------------|---------|
| Chamouni (3000 feet) . . . | 0.063 | 20.894 |
| Grands Mulets (11,000 feet) . . | 0.111 | 20.802 |
| Mont Blanc (15,732 feet) . . . | 0.061 | 20.963 |

A litre of pure and dry air at 00° C. and 760 mm. pressure weighs 1.29366 grams. 100 cubic inches at 15.50° C. (60° F.) and 30 inches barom. weigh 30.935 grains: hence a cubic foot weighs 536.96 grains, which is $\frac{1}{8}\frac{1}{2}$ of the weight of a cubic foot of water at the same temperature.

The analysis of air is very well effected by passing it over finely divided copper contained in a tube of hard glass, carefully weighed and then heated to redness: the nitrogen is suffered to flow into an exhausted glass globe, also previously weighed. The increase in weight of the copper after the experiment gives the amount of oxygen, and the increase in weight of the exhausted globe gives the nitrogen.

Fig. 104.



An easier but less accurate method consists in introducing into a graduated tube, standing over water, a known quantity of the air to be examined, and then passing into the latter a stick of phosphorus affixed to the end of a wire. The whole is left about twenty-four hours, during which the oxygen is slowly but completely absorbed, after which the phosphorus is withdrawn, and the residual gas read off.

Liebig proposed the use of an alkaline solution of pyrogallie acid (a substance which will be described in the department of organic chemistry) for the absorption of oxygen. The absorptive power of such a solution, which turns deep black on coming in contact with the oxygen, is very considerable. Liebig's method combines great accuracy with unusual rapidity and facility of execution.

Another plan is to mix the air with hydrogen and pass an electric spark through the mixture: after explosion the volume of gas is read off and compared with that of the air employed.

Fig. 105.



Since the analysis of gaseous bodies by explosion is an operation of great importance, it may be worth while to describe the process in detail, as it is applicable, with certain obvious variations, to a number of analogous cases.

Instruments for this purpose are called eudiometers. The simplest, and, on the whole, the most convenient, consists of a straight graduated glass tube (fig. 105) closed at the top, and having platinum wires inserted near the closed end, to give passage to an electric spark. This tube is filled with mercury, and inverted in a mercurial pneumatic trough.

For the analysis of air, a quantity sufficient to fill about one-sixth of the tube is introduced, and its volume ac-

separately ascertained by reading off with a telescope the number of the divisions on the tube to which the mercury reaches, whilst the height of the column of mercury in the tube above the trough, together with that of the barometer, and the temperature of the air, are also read off. A quantity of pure hydrogen gas is now added, more than sufficient to unite with all the oxygen present (about half the volume of the air), and the volume of the gas and the pressure exerted upon it, are determined as before. An electric spark is now passed through the mixture, care being taken to prevent any escape, by pressing the open end of the eudiometer against a piece of sheet caoutchouc under the mercury in the trough. After the explosion, the volume is again determined, and is found to be less than that before the explosion. The volume of gas read off must in each case be reduced to standard pressure and temperature by the method already given (p. 49).

Now, since the hydrogen is in excess, and 2 volumes of that gas unite with 1 volume of oxygen to form water, one-third of the diminution must be the volume of the oxygen contained in the air introduced. An example will render this clear:—

Air introduced 100 measures.

Air and hydrogen 100

Volume after explosion 97

Diminution 63

$$\frac{63}{3} = 21 = \text{oxygen in the 100 measures.}$$

Compounds of Nitrogen and Oxygen.

There are five distinct compounds of nitrogen and oxygen, thus named and constituted:—

| | Formula. | Composition. | | | |
|----------------------------|----------------------|--------------|---------|------------|---------|
| | | By weight | | By volume. | |
| | | Nitrogen. | Oxygen. | Nitrogen. | Oxygen. |
| Monoxide | N_2O | 28 | 16 | 2 | 1 |
| Dioxide | N_2O_2 , or NO | 28 | 32 | 2 | 2 |
| Trioxide, or Nitrous oxide | N_2O_3 | 28 | 48 | 2 | 3 |
| Tetroxide | N_2O_4 , or NO_2 | 28 | 64 | 2 | 4 |
| Pentoxide, or Nitric oxide | N_2O_5 | 28 | 80 | 2 | 5 |

A comparison of these numbers will show that the quantities of oxygen which unite with a given quantity of nitrogen are to one another in the ratio of the numbers 1, 2, 3, 4, 5.

The first, third, and fifth of the compounds in the table are capable of taking up the elements of water and of metallic oxides to form salts (p. 125), called respectively hyponitrites, nitrites, and nitrates, the hydrogen salts being also called hyponitrous, nitrous, and nitric acid.

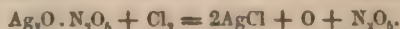
The composition of these acids and of their potassium salts is represented by the following formulæ:—

| | |
|---|--|
| Hydrogen hyponitrite, or Hyponitrous acid | $\text{H}_2\text{O.N}_2\text{O}$ or HNO |
| Potassium hyponitrite | $\text{K}_2\text{O.N}_2\text{O}$ or KNO |
| Hydrogen nitrite, or Nitrous acid | $\text{H}_2\text{O.N}_2\text{O}_2$ or HNO_2 |
| Potassium nitrite | $\text{K}_2\text{O.N}_2\text{O}_2$ or KNO_2 |
| Hydrogen nitrate, or Nitric acid | $\text{H}_2\text{O.N}_2\text{O}_3$ or HNO_3 |
| Potassium nitrate | $\text{K}_2\text{O.N}_2\text{O}_3$ or KNO_3 |

The dioxide and tetroxide of nitrogen do not form salts.

It will be convenient to commence the description of these compounds with the last on the list, viz., the pentoxide, as its salts, the nitrates, are the sources from which all the other compounds in the series are obtained.

Nitrogen Pentoxide, or Nitric Oxide, N_2O_5 (also called *Anhydrous Nitric Acid*, or *Nitric Anhydride*).—This compound was discovered in 1849 by Deville, who obtained it by exposing silver nitrate to the action of chlorine gas. Chlorine and silver then combine, forming silver chloride, which remains in the apparatus, while oxygen and nitrogen pentoxide separate:



It may also be prepared by slowly distilling pure and highly concentrated nitric acid at a blood-heat with phosphoric oxide, a substance which has a very powerful attraction for water. The distillate consists of two layers of liquid, the upper of which is nitrogen pentoxide mixed with nitrous and nitric acids; and on separating this upper layer, and cooling it with ice or a freezing mixture, the pentoxide separates in crystals.

Nitrogen pentoxide is a colorless substance, crystallizing in six-sided prisms, which melt at 30°C . (86°F .), and boil between 45° and 50°C . (113° – 122°F .), when they begin to decompose. Its specific gravity in the solid state is above 1.64; in the liquid state below 1.636. Nitrogen pentoxide sometimes explodes spontaneously. It dissolves in water with great rise of temperature, forming hydrogen nitrate or nitric acid. It also unites with a smaller proportion of water, forming the *hemihydrate* $2\text{N}_2\text{O}_5.\text{H}_2\text{O}$, which constitutes the chief part of the lower layer of the distillate obtained in the manner just described. It is liquid at ordinary temperatures, but crystallizes in a freezing mixture.

NITRATES—NITRIC ACID.—In certain parts of India, and in other hot dry climates where rain is rare, the surface of the soil is occasionally covered by a saline efflorescence, like that sometimes apparent on newly plastered walls; this substance collected, dissolved in hot water, and crystallized from the filtered solution, furnishes the highly important salt known in commerce as nitre or saltpetre, and consisting of potassium nitrate. To obtain nitric acid, equal weights of powdered nitre and strong sulphuric acid are introduced into a glass retort, and heat is applied by means of a gas-lamp or charcoal chausser. A flask, cooled by a wet cloth, is adapted to the retort to serve for a receiver. No luting of any kind must be used.

As the distillation advances, the red fumes which first arise disappear, but towards the end of the process they again become manifest. When this happens, and very little liquid passes over, while the greater part of the saline matter of the retort is in a state of tranquil fusion, the operation may be stopped; and when the retort is quite cold, water may be introduced to dissolve out the saline residue. The reaction consists in an interchange between the potassium of the nitre and half the hydrogen of the sulphuric acid (hydrogen sulphate), whereby there are formed hydro-

potassium nitrate which distills over, and hydrogen and potassium sulphate which remains in the retort.



In the manufacture of nitric acid on the large scale, the glass retort is replaced by a cast-iron cylinder, and the receiver by a series of earthen condensing vessels connected by tubes. Sodium nitrate, found native in Peru, is now generally substituted for potassium nitrate.

Nitric acid thus obtained has a specific gravity of from 1.5 to 1.52; it has a golden-yellow color, due to nitrogen trioxide, or tetroxide, which is held in solution, and, when the acid is diluted with water, gives rise by its decomposition to a disengagement of nitrogen dioxide. Nitric acid is exceedingly corrosive, staining the skin deep yellow, and causing total disorganization. Poured upon red-hot powdered charcoal, it causes brilliant combustion; and when added to warm oil of turpentine, acts upon that substance so energetically as to set it on fire.

Pure nitric acid, in its most concentrated form, is obtained by mixing the above with about an equal quantity of strong sulphuric acid, redistilling, collecting apart the first portion which comes over, and exposing it, in a vessel slightly warmed and sheltered from the light, to a current of dry air made to bubble through it, which completely removes the nitrous acid. In this state the product is as colorless as water; it has the sp. gr. 1.517 at 15.5° C. (60° F.), boils at 84.5° (184° F.), and consists of 54 parts nitrogen pentoxide and 9 parts water. Although nitric acid in a more dilute form acts very violently upon many metals, and upon organic substances generally, this is not the case with the most concentrated acid; even at a boiling heat, it refuses to attack iron or tin; and its mode of action on lignin, starch, and similar substances, is quite peculiar, and very much less energetic than that of an acid containing more water.

On boiling nitric acid of different degrees of concentration, at the ordinary atmospheric pressure, a residue is left, boiling at 120.5° C. (248.9° F.) and 2½ inches barometer, and having the sp. gr. 1.414 at 15.5° C. This acid was formerly supposed to be a definite compound of nitric acid with water, but Roscoe has recently proved this assumption to be incorrect, the composition of the acid varying according to the pressure under which the liquid boils.

The nitrates form a very extensive and important group of salts, which are remarkable for being all soluble in water. Hydrogen nitrate is of great use in the laboratory, and in many branches of industry.

The acid prepared in the way described is apt to contain traces of chlorine from common salt in the nitre, and sometimes of sulphate from accidental splashing of the pasty mass in the retort. To discover these impurities, a portion is diluted with four or five times its bulk of distilled water, and divided between two glasses. Solution of silver nitrate is dropped into the one, and solution of barium nitrate into the other; if no change ensue in either case the acid is free from the impurities mentioned.

Nitric acid has been formed in small quantity, by passing a series of electric sparks through a portion of air in contact with water or an alkaline solution. The amount of acid so formed after many hours is very minute; still it is not impossible that powerful discharges of atmospheric electricity may sometimes occasion a trifling production of nitric acid in the air. A very minute quantity of nitric acid is produced by the combustion of hydrogen and other substances in the atmosphere; it is also formed by the oxidation of ammonia.

Nitric acid is not so easily detected in solution in small quantities as many

other acids. Owing to the solubility of all its compounds, no precipitant can be found for this acid. A good mode of testing it is based upon its power of bleaching a solution of indigo in sulphuric acid when boiled with that liquid. The absence of chlorine must be insured in this experiment by means which will hereafter be described; otherwise the result is equivocal.

The best method for the detection of nitric acid is the following: The substance to be examined is boiled with a small quantity of water, and the solution cautiously mixed with an equal volume of concentrated sulphuric acid; the liquid is then allowed to cool, and a strong solution of ferrous sulphate carefully poured upon it, so as to form a separate layer. If large quantities of nitric acid are present, the surface of contact first, and then the whole of the liquid, becomes black. If but small quantities of nitric acid are present, the liquid becomes reddish-brown or purple. The ferrous sulphate reduces the nitric acid to nitrogen dioxide, which, dissolving in the solution of ferrous sulphate, imparts to it a dark color.

Nitrogen Monoxide, N_2O (sometimes called *Nitrous Oxide*; also *Laughing Gas*).—When solid ammonium nitrate is heated in a retort or flask* (fig. 106), furnished with a perforated cork and bent tube, it is resolved into water and nitrogen monoxide, $NH_4NO_3 = 2H_2O + N_2O$.

No particular precaution is required in the operation, save due regulation of the heat, and the avoidance of tumultuous disengagement of the gas.

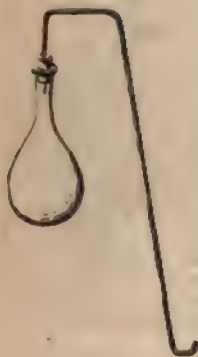
Nitrogen monoxide is a colorless, transparent, and almost inodorous gas, of distinctly sweet taste. Its specific gravity is 1.525; a litre of it weighs 1.97172 gram; 100 cubic inches weigh 47.29 grains. It supports the combustion of a taper or a piece of phosphorus with almost as much energy as pure oxygen: it is easily distinguished, however, from that gas by its solubility in cold water, which dissolves nearly its own volume: hence it is necessary to use tepid water in the pneumatic trough or gas-holder, otherwise great loss of gas will ensue.

Gaseous nitrogen monoxide mixed with an equal volume of hydrogen, and fired by the electric spark in the eudiometre, explodes with violence, and liberates its own measure of nitrogen. Every two volumes of the gas must consequently contain two volumes of nitrogen and one volume of oxygen, the whole condensed or contracted one-third—a constitution resembling that of vapor of water.

The most remarkable property of this gas is its intoxicating power upon the animal system. If quite pure, or merely mixed with atmospheric air it may be respired for a short time without danger or inconvenience. The effect is very transient, and is not followed by depression. The gas is now much used as an anæsthetic in dental surgery.

Nitrogen monoxide has been liquefied, but with difficulty; it requires, at $7.2^\circ C.$ ($45^\circ F.$), a pressure of 50 atmospheres: the liquid monoxide

Fig. 103.



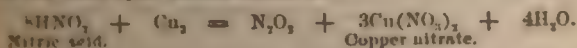
* Florence oil-flasks, which may be purchased at a very trifling sum, constitute exceedingly useful vessels for chemical purposes, and often supersede retorts or other expensive apparatus. They are rendered still more valuable by cutting the neck smoothly round with a hot iron, softening it in the flame of a good Argand gas-lamp, or Bunsen burner, and then turning over the edge so as to form a lip or border. The neck will then bear a tightly-fitting cork without risk of splitting.

a specific gravity of 0.9004; it is not miscible with water. Faraday effected it by exposing it in a sealed tube to the cold produced by a mixture of solid carbonic acid and ether, but he supposed that it could not be effected by the cold produced by its own evaporation. This, however, is effected if the evaporation be accelerated by a strong current of air. A very fine steel tube is directed into the axis of a thin brass cone, having a small opening, about the eighth of an inch, at its apex. On passing a stream of the liquid to issue from the jet, it is retained in the tube for a moment, and then forcibly blown out at the apex, together with a strong stream of air. The solid is in this way formed in some quantity, and may be collected in a dish lined with filter-paper, or other suitable material. Solid nitrogen monoxide is more compact in appearance than solid carbonic acid, and, unlike the latter, it melts and boils, if gently warmed, passing into the gaseous state: hence, if placed in contact with the flame it produces a painful blister, like a burn. The melting or freezing point of the monoxide is -120° F. or -99° C., and its boiling point -186° F. or -92° C. It is the proximity of the boiling and freezing points which renders it possible to freeze the liquid by simply blowing air through it.*

HYPONITROUS ACID, $N_2O.H_2O$, or HNO .—When a solution of sodium nitrate, $NaNO_3$, or ammonium nitrate, $NH_4.NO_3$, is treated with sodium amalgam (a compound of sodium and mercury), the nitrate gives up 2 volumes of oxygen to the sodium, and is reduced to hyponitrite, $NaNO$. On neutralizing the excess of alkali in the liquid, by adding acetic acid till the solution no longer gives a brown or black precipitate (of silver oxide) with silver nitrate, a solution of sodium hyponitrite is obtained, which is claimed to test-paper, and gives with silver nitrate a yellow precipitate of silver hyponitrite, $AgNO$. When the original alkaline liquid is acidified with acetic acid, and heated, the hyponitrous acid is resolved into water and nitrogen monoxide, which escapes as gas, $2HNO = H_2O + N_2O$.†

Nitrogen Dioxide, N_2O_2 , or NO (sometimes called *Nitric Oxide*).—Copper wire or turnings of copper are put into the apparatus employed for preparing hydrogen (p. 130), together with a little water, and nitric acid poured by the funnel until brisk effervescence is excited. The gas may be collected over cold water, as it is not sensibly soluble.

The reaction is a simple deoxidation of some of the nitric acid by the metal: the metal is oxidized, and the oxide so formed is dissolved by another portion of the acid, forming copper nitrate. Nitric acid is very prone to act thus upon certain metals:—



The gas obtained in this manner is colorless and transparent: in contact with air or oxygen gas it produces deep red fumes, which are readily absorbed by water: this character is sufficient to distinguish it from all other gaseous bodies. A lighted taper plunged into the gas is extinguished: lighted phosphorus, however, burns in it with great brilliancy.

The specific gravity of nitrogen dioxide is 1.039; a litre weighs 1.34343 grams. It contains equal measures of oxygen and nitrogen gases united without condensation. When this gas is passed into the solution of a ferrous salt, it is absorbed in large quantity, and a deep brown, or nearly

* Wille, Chem. Soc. Journ. 1874, p. 21

† Davy's, Proceedings of the Royal Society, xix. 426; Chem. Soc. Journ., 1871, p. 434

black liquid produced, which seems to be a definite compound of the two substances (p. 154). The compound is decomposed by boiling.

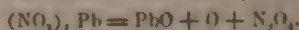
Nitrogen Trioxide, or Nitrous Oxide, N_2O_3 .—When four measures of nitrogen dioxide are mixed with one measure of oxygen, and the gases, perfectly dry, are exposed to a temperature of -18° , they condense to a thin mobile blue liquid, which emits orange-red vapors.

Nitrogen trioxide, sufficiently pure for most purposes, is obtained by pouring concentrated nitric acid on lumps of arsenious acid, and gently warming the mixture, in order to start the reaction. The trioxide is then evolved as an orange-red gas, arsenic acid remaining behind.

Nitrogen trioxide is decomposed by water, being converted into nitric acid and nitrogen dioxide: $3N_2O_3 + H_2O = 2HNO_3 + 2N_2O_2$. For this reason it cannot be made to unite directly with metallic oxides; potassium nitrite may, however, be prepared by fusing potassium nitrate, whereby part of its oxygen is driven off; and many other salts of nitrous acid may be obtained by indirect means. Thus a solution of potassium or sodium nitrite may be prepared by passing the vapor of nitrogen trioxide, obtained as above by heating nitric acid with arsenious acid (or with starch), into a solution of caustic potash or soda.

Nitrogen Tetroxide, N_2O_4 or NO_2 , also called Nitric Peroxide.—This is the principal constituent of the deep red fumes always produced when nitrogen dioxide escapes into the air.

It may be obtained in the pure state:—1. By exposing a mixture of 2 vols. nitrogen dioxide and 1 vol. oxygen incorporated by passing through a tube filled with broken porcelain, and thoroughly dried by transmission over pumice soaked in oil of vitriol and then over recently fused stick potash, to the action of a freezing mixture of salt and ice; the tetroxide condenses in transparent crystals, or if the slightest trace of moisture is present, into an almost colorless liquid. 2. By the direct combination of oxygen with the trioxide, as when a stream of oxygen is passed into the mixture of the trioxide and other oxides of nitrogen evolved by the action of fuming nitric acid on arsenious acid. The liquid tetroxide thus obtained is pure enough for most purposes after one distillation. 3. By heating thoroughly dried lead nitrate in a retort, whereby a mixture of tetroxide and oxygen is evolved, the former of which may be condensed as above, while the latter passes on.—



The first portions of nitrogen tetroxide thus obtained do not solidify, doubtless owing to the presence of a trace of moisture, but if the receiver be changed in the midst of the operation, and if every care has been taken to avoid moisture, the later portions may be obtained in the crystalline form.

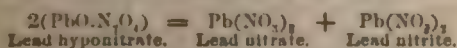
Nitrogen tetroxide at very low temperatures forms transparent, colorless, prismatic crystals which melt at -9° F., but when once melted do not resolidify till cooled down to -30° . Above -9° it forms a mobile liquid of specific gravity 1.451, the appearance of which varies greatly according to the temperature. When still liquid below -9° , it is almost colorless; at -9° it has a perceptible greenish-yellow tint; at 0° the color is some what more marked; at 10° it is decidedly yellow; and at 15° and upwards orange-yellow, the depth of color increasing progressively with the temperature up to 22° , the boiling point of the liquid. The vapor has a brown-red color, the depth of which also increases with the temperature, until at 46° it is so dark as to be almost opaque. This remarkable change of color

is accompanied by a great diminution of density as the temperature rises, such phenomena pointing to a molecular change produced in the vapor by heat. Messrs. Playfair and Wanklyn have determined the density of the vapor by Dumas' method, using nitrogen as a diluent (p. 68), and find that the densities at different temperatures are as follows:—

| Temperature. | Vapor-density. |
|-----------------|----------------|
| 97.5° | 1.783 |
| 24.5 | 2.520 |
| 11.3 | 2.645 |
| 4.2 | 2.588 |

The vapor is absorbed by strong nitric acid, which thereby acquires a yellow or red tint, passing into green, then into blue, and afterwards disappearing altogether on the addition of successive portions of water. The deep red fuming acid of commerce, called *nitrous acid*, is simply nitric acid impregnated with nitrogen tetroxide.

Nitrogen tetroxide is decomposed by water at very low temperatures in such a manner as to yield nitric and nitrous acids, $\text{N}_2\text{O}_4 + \text{H}_2\text{O} = \text{HNO}_3 + \text{HNO}_2$, but when added to excess of water at ordinary temperatures it yields nitric acid, and the products of decomposition of nitrous acid, namely, nitric acid and nitrogen dioxide. In like manner, when passed into alkaline solutions, it forms a nitrate and a nitrite of the alkali-metal; but it has been also supposed to unite directly, under certain circumstances, with metallic oxides—lead oxide, for example—forming definite crystalline salts, and has hence been called *hyponitric acid*; but it is most probable that these salts are compounds of nitrates and nitrites: *e. g.*,



Nitrogen appears to combine, under favorable circumstances, with metals. When iron is heated to redness in an atmosphere of ammonia, it becomes brittle and crystalline, and shows an increase in weight, said to vary from 8 to 12 per cent.; while, according to other observers, the physical characters of the metal are changed without sensible alteration of weight. By heating copper in ammonia, no compound of nitrogen with copper is produced, but when ammonia is passed over copper oxide heated to 300°, water is formed, and a soft brown powder produced, which, when heated further, evolves nitrogen, and leaves metallic copper. The same effect is produced by the contact of strong acids. A similar compound of chromium with nitrogen appears to exist.

NITROGEN AND HYDROGEN; AMMONIA, NH_3 .

When powdered sal-ammoniac is mixed with moist calcium hydrate (slaked lime), and gently heated in a glass flask, a large quantity of gaseous matter is disengaged, which must be collected over mercury, or by displacement, advantage being taken of its low specific gravity.

Ammonia gas thus obtained is colorless; it has a strong pungent odor, and possesses in an eminent degree those properties to which the term *alkaline* is applied; that is to say, it turns the yellow color of turmeric to brown, that of reddened litmus to blue, and combines readily with acids, neutralizing them completely; by these reactions it is easily distinguished from all other bodies possessing the same physical characters. Under a pressure of 6.5 atmospheres at 15.5° C. (60° F.), ammonia condenses to the liquid form. Water dissolves about 700 times its volume of this gas, forming a solution which, in a more dilute state, has long been known

under the name of *liquor ammoniac*; by heat a great part is again expelled. The solution is decomposed by chlorine, sal-ammoniac being formed, and nitrogen set free.

Ammonia has a density of 0.589; a litre weighs 0.76271 gram. It can not be formed by the direct union of its elements, although it is sometimes produced under rather remarkable circumstances by the deoxidation of nitric acid.* The great sources of ammonia are the feebly compounded azotised principles of the animal and vegetable kingdoms, which, when left to putrefactive change, or subjected to destructive distillation, almost invariably give rise to an abundant production of this substance.

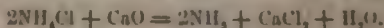
The analysis of ammonia gas is easily effected. When a portion is confined in a graduated tube over mercury, and electric sparks are passed through it for a considerable time, the volume of the gas gradually increases until it becomes doubled. On examination, the tube is found to contain a mixture of 3 measures of hydrogen gas and 1 measure of nitrogen. Every two volumes of the ammonia, therefore, contained three volumes of hydrogen and one of nitrogen, the whole being condensed to one-half. The weight of the two constituents is in the proportion of 3 parts hydrogen to 14 parts nitrogen.

Ammonia may also be decomposed into its elements by transmission through a red-hot tube.

Solution of ammonia is a very valuable reagent, and is employed in a great number of chemical operations, for some of which it is necessary to have it perfectly pure. The best mode of preparation is the following —

Equal weights of sal-ammoniac (NH_4Cl), and quicklime (CaO), are taken; the lime is slaked in a covered basin, and the salt reduced to powder. These are mixed and introduced into a large flask connected with a wash-bottle and a receiver containing water, in the manner which will be described in connection with hydrochloric acid (fig. 122). A little water is added to the mixture, just enough to dampen it and cause it to aggregate into lumps. On cautiously applying heat to the flask, ammonia is disengaged very regularly and uniformly, and condenses in the water of the receiver. Calcium chloride (CaCl_2), with excess of calcium hydrate (slaked lime), remains in the flask.

The decomposition of the salt is represented by the equation. —



Solution of ammonia should be perfectly colorless, leave no residue on evaporation, and when supersaturated by nitric acid, give no cloud or muddiness with silver nitrate. Its density diminishes with its strength, that of the most concentrated being about 0.875. The value in alkali of any sample of liquor ammoniac is most safely inferred, not from a knowledge of its density, but from the quantity of acid a given amount will saturate. The mode of conducting this experiment will be described under *Alkalimetry*.

When solution of ammonia is mixed with acids of various kinds, salts are generated, which resemble in the most complete manner the corresponding potassium and sodium compounds; they are best discussed in connection with the latter. The ammonia salts may be regarded either as direct compounds of ammonia, NH_3 , with acids (HCl , for example), or as resulting from the replacement of the hydrogen of an acid by the group NH_4 , called *ammonium*, which in this sense is a compound metal, chemically equivalent to potassium, sodium, silver, etc. Thus, —

* A mode of converting the nitrogen of the atmosphere into ammonia, by a succession of chemical operations, will be noticed in connection with Cyanogen under *Organic Chemistry*.

| | | | | |
|-----------------------|---|-----|-------------------------------------|--------------------|
| Ammonia hydrochloride | $\text{NH}_3 \cdot \text{HCl}$ | $=$ | $\text{NH}_4 \cdot \text{Cl}$ | Ammonium chloride. |
| " nitrate | $\text{NH}_3 \cdot \text{HNO}_3$ | $=$ | $\text{NH}_4 \cdot \text{NO}_3$ | " nitrate. |
| " sulphate | $(\text{NH}_3)_2 \cdot \text{H}_2\text{SO}_4$ | $=$ | $(\text{NH}_4)_2 \cdot \text{SO}_4$ | " sulphate. |

The formulae in the second column are exactly analogous to those of the potassium salts, KCl , KNO_3 , K_2SO_4 .

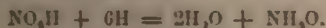
The aqueous solution of ammonia may be supposed to contain the hydrate of ammonium $\text{NH}_3 \cdot \text{HO}$; but this compound is not known in the solid state.

Any ammoniacal salt can at once be recognized by the evolution of ammonia which takes place when it is heated with slaked lime, or solution of potash or soda.

HYDROXYLAMINE, NH_2O .

This compound, intermediate in composition between ammonia NH_3 , and ammonium hydrate $\text{NH}_4 \cdot \text{HO}$, is formed by the direct union of hydrogen with nitrogen dioxide: $\text{NO} + \text{H}_2 = \text{NH}_2\text{O}$, and may be prepared by passing nitrogen dioxide through a series of flasks in which hydrogen is evolved by heating hydrochloric acid with tin. The resulting liquid is freed from tin by hydrogen sulphide; the filtered liquid evaporated to dryness; the residue washed with cold alcohol, and digested with boiling alcohol; the alcoholic solution mixed with platinic chloride to precipitate sal-ammoniac, and the filtered alcoholic liquid mixed with ether, which throws down pure hydrochloride of hydroxylamine.

Hydroxylamine is also formed by the action of hydrogen (evolved as above) on nitric acid or ethyl nitrate:



Hydroxylamine is a very volatile and easily decomposable base, and can be obtained only in solution. Its salts are decomposed by potash, with evolution of nitrogen and formation of ammonia, quickly in concentrated, gradually in dilute solutions. Solutions of hydroxylamine may, however, be obtained by decomposing the salts in other ways, an alcoholic solution, for example, by decomposing the nitrate dissolved in alcohol with alcoholic potash. Alkaline carbonates also separate hydroxylamine, with evolution of carbon dioxide. The solutions have an alkaline reaction, and precipitate many metallic salts; with the salts of lead, iron, nickel, and zinc, and with chrome-alum and common alum, they form precipitates insoluble in excess of hydroxylamine. With aqueous cupric sulphate, hydroxylamine forms a grass-green precipitate, which when boiled with water, is reduced, with evolution of gas, to cuprous oxide; an ammoniacal cupric solution is decolorized by it. Mercuric chloride is reduced to mercurous chloride, and if the hydroxylamine is in excess, to metallic mercury. Silver solutions yield a black precipitate, which is quickly reduced, with evolution of gas, to metallic silver. Hydroxylamine also reduces acid potassium chromate. In many of these reactions the hydroxylamine appears to be completely decomposed, with formation of nitrogen or its monoxide.

The salts of hydroxylamine decompose when heated, with copious and sudden evolution of gas; most of them easily from supersaturated solutions. None of those yet examined contain water of crystallization. The hydrochloride, $\text{NH}_2\text{O} \cdot \text{HCl}$, crystallizes from alcohol in long spicular crystals resembling urea; from water in large irregular six-sided tables; it melts at 108° , and then decomposes, with violent evolution of gas, into nitrogen, hydrochloric acid, water, and sal-ammoniac. The nitrate, $\text{NH}_2\text{O} \cdot \text{HNO}_3$, distils slowly by spontaneous evaporation to a radio-crystalline, very deliquescent mass, easily soluble in absolute alcohol, decomposing at 100° .

CARBON.

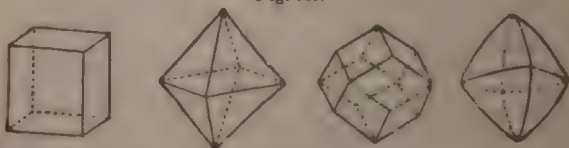
Atomic weight, 12. Symbol, C.

This substance occurs in a state of purity, and crystallized, in two distinct and very dissimilar forms—namely, as diamond, and as graphite or plumbago. It constitutes a large proportion of all organic structures, animal and vegetable: when these latter are exposed to destructive distillation in close vessels, a great part of their carbon remains, obstinately retaining some of the hydrogen and oxygen, and associated with the earthy and alkaline matter of the tissue, giving rise to the many varieties of charcoal, coke, etc. This residue, when perfectly separated from foreign matter, constitutes a third variety of carbon.

The diamond is one of the most remarkable substances known; long prized on account of its brilliancy as an ornamental gem, the discovery of its curious chemical nature confers upon it a high degree of scientific interest. Several localities in India, the Island of Borneo, South Africa, and Brazil, furnish this beautiful substance. It is always distinctly crystallized, often quite transparent and colorless, but now and then having a shade of yellow, pink, or blue. The origin and true geological position of the diamond are unknown; it is always found imbedded in gravel and transported materials whose history cannot be traced. The crystalline form of the diamond is that of the regular octohedron or cube, or some figure geometrically connected with these. Many of the octohedral crystals exhibit a very peculiar appearance, arising from the faces being curved or rounded, which gives to the crystal an almost spherical figure.

The diamond is infusible and unalterable even by a very intense heat, provided air be excluded; but when heated, thus protected, between the poles of a strong galvanic battery, it is converted into coke or graphite; heated to whiteness in a vessel of oxygen, it burns with facility, yielding carbonic acid gas.

Fig. 107.



The diamond is the hardest substance known: it admits of being split or cloven without difficulty in particular directions, but can only be cut or abraded by a second portion of the same material; the powder rubbed off in this process serves for polishing the new faces, and is also highly useful to the lapidary and seal-engraver. One very curious and useful application of the diamond is made by the glazier: a *foi-tant* of this mineral, like a bit of flint, or any other hard substance, scratches the surface of the glass; a *crystal* of diamond, having the rounded octohedral figure spoken of, held in one particular position on the glass—namely, with an edge formed by the meeting of two adjacent faces presented to the surface—and then drawn along with gentle pressure, causes a split or cut, which penetrates to a considerable depth into the glass, and determines its fracture with perfect certainty.

Graphite or plumbago appears to consist essentially of pure carbon,

although most specimens contain iron, the quantity of which varies from a mere trace up to five per cent. Graphite is a somewhat rare mineral; the finest and most valuable for pencils was formerly obtained from Borrowdale, in Cumberland, where a kind of irregular vein is found traversing the ancient slate beds of that district, but the mine is now nearly exhausted. Large quantities of graphite are imported from Germany, the East Indies, and the United States.* Crystals are not common: when they occur, they have the figure of a short six-sided prism—a form bearing no geometric relation to that of the diamond.

Graphite is often formed artificially in certain metallurgic operations: the brilliant scales which sometimes separate from melted cast-iron on cooling, called by the workmen "kish," consist of graphite.

Lump-black, the soot produced by the imperfect combustion of oil or coal, is the best example that can be given of carbon in its uncrystallized or amorphous state. To the same class belong the different kinds of charcoal. That prepared from wood, either by distillation in a large iron retort, or by the smothered combustion of a pile of fagots partially covered with earth, is the most valuable as fuel. Coke, the charcoal of pit-coal, is much more impure; it contains a large quantity of earthy matter, and very often sulphur, the quality depending very much upon the mode of preparation. Charcoal from bones and animal matters in general is a very valuable substance, on account of the extraordinary power it possesses of removing coloring matters from organic solutions; it is used for this purpose by the sugar-refiner to a very great extent, and also by the manufacturing and scientific chemist. The property in question is possessed by all kinds of charcoal in a small degree.

Charcoal made from box, or other dense wood, has the property of condensing gases and vapors into its pores; of ammoniacal gas it is said to absorb not less than ninety times its volume, while of hydrogen it takes up less than twice its own bulk, the quantity being apparently connected with the property in the gas of suffering liquefaction. This property of absorbing gases, as well as the decolorizing power, no doubt depends in some way upon the same peculiar action of surface so remarkable in the case of platinum in a mixture of oxygen and hydrogen. The absorbing power is, indeed, considerably increased by saturating charcoal with solution of platinum, and subsequently igniting it, so as to coat the charcoal with a thin film of platinum. Dr. Stenhouse, who suggested this plan, holds that the gases thus absorbed undergo a kind of oxidation within the pores of the charcoal.

Compounds of Carbon and Oxygen.

There are two direct inorganic compounds of carbon and oxygen, called carbon monoxide and carbon dioxide; their composition may be thus stated:—

* The graphite which can be directly cut for pencils occurring only in limited quantity powdered graphite, obtained from the inferior varieties of the mineral, is now frequently consolidated for this purpose. The mechanical division of graphite presents considerable difficulties, which may be entirely obviated by adopting a chemical process suggested by Sir Benjamin Brodie, applicable, however, only to certain varieties, such as Ceylon and Siberian graphite. This process consists in introducing the coarsely powdered graphite, previously mixed with $\frac{1}{10}$ of its weight of potassium chlorate, into 2 parts of concentrated sulphuric acid, which is heated in a water bath until the evolution of acid fumes ceases. The acid is then removed by water, and the graphite dried. Thus prepared, this substance, when heated to a temperature approaching a red heat, swells up to a bulky mass of finely divided graphite.

| | | By weight. | |
|---------------------------------|---------|------------|---------|
| | | Carbon. | Oxygen. |
| Carbon monoxide, CO | | 12 | 16 |
| Carbon dioxide, CO ₂ | | 12 | 32 |

Carbon Dioxide or Carbonic Anhydride—(commonly called *Carbonic Acid*), is always produced when charcoal burns in air or oxygen gas: it is most conveniently obtained, however, by decomposing a carbonate with one of the stronger acids. For this purpose the apparatus for generating hydrogen (p. 130), may again be employed: fragments of marble are put into the bottle with enough water to cover the extremity of the funnel-tube, and hydrochloric or nitric acid is added by the latter, until the gas is freely disengaged. Chalk-powder and dilute sulphuric acid may be used instead. The gas may be collected over water, although with some loss; or very conveniently by displacement, if it be required dry, as shown in fig. 108. The long drying-tube is filled with fragments of calcium chloride, and the heavy gas is conducted to the bottom of the vessel in which it is to be received, the mouth of the latter being lightly closed.*

Fig. 108.



Carbon dioxide is a colorless gas; it has an agreeable pungent taste and odor, but cannot be respired for a minute without insensibility following. Its specific gravity is 1.524; a litre weighs 1.96664 grams, and 100 cubic inches weigh 47.26 grains.

This gas is very hurtful to animal life, even when largely diluted with air; it acts as a narcotic poison: hence the danger arising from imperfect ventilation, the use of fire-places and stoves of all kinds unprovided with proper chimneys, and the crowding together of many individuals in houses and ships without efficient means for renewing the air: for carbon dioxide is constantly disengaged during the process of respiration, which, as already mentioned (p. 124), is nothing but a process of slow combustion. This gas is sometimes emitted in large quantity from the earth in volcanic districts, and it is constantly generated where organic matter is in the act of undergoing fermentive decomposition. The fatal "after-damp" of the coal-mines contains a large proportion of carbon dioxide.

A lighted taper plunged into carbon dioxide is instantly extinguished

* In connecting tube-apparatus for conveying gases or cold liquids, not corrosive, tubes of vulcanized caoutchouc, which are now articles of commerce, are very serviceable. Glass tubes are easily bent in the flame of a spirit-lamp, or a Bunsen burner, and, when necessary, cut by scratching with a file and broken asunder.

even to the red-hot snuff. The gas, when diluted with three times its volume of air, still retains the power of extinguishing a light. It is easily disengaged from nitrogen, which is also incapable of supporting combustion, by its rapid absorption by caustic alkali, or by lime-water: the turbidity communicated to the latter from the production of insoluble calcium carbonate is very characteristic.

Cold water dissolves about its own volume of carbon dioxide, whatever be the density of the gas with which it is in contact (comp. p. 146): the solution temporarily reddens litmus paper. In common soda-water, and in effervescent wines, examples may be seen of the solubility of the gas. Boiling water absorbs a perceptible quantity.

Some of the interesting phenomena attending the liquefaction of carbon dioxide have been already described (p. 64): it requires for the purpose a pressure of 38.5 atmospheres at 0°. The liquefied oxide is colorless and limpid, lighter than water, and four times more expansible than air; it mixes in all proportions with ether, alcohol, naphtha, oil of turpentine, and carbon disulphide, and is insoluble in water and fat oils. In this condition it does not exhibit any of the properties of an acid.

Carbon dioxide exists, as already mentioned, in the air: relatively its quantity is but small; but absolutely, taking into account the vast extent of the atmosphere, it is very great, and fully adequate to the purpose of supplying plants with their carbon, these latter having the power, by the aid of their green leaves, of decomposing carbon dioxide, retaining the carbon, and expelling the oxygen. The presence of light is essential to this effect, but of the manner in which it is produced we are yet ignorant.

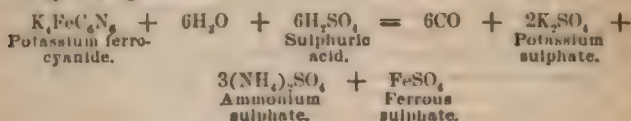
The carbonates form a very large and important group of salts, some of which, as the carbonates of calcium and magnesium, occur very abundantly in nature. They contain the elements of carbon dioxide and a metallic oxide: calcium carbonate, for example, being composed of 56 parts of calcium oxide or lime, and 44 parts by weight of carbon dioxide, or of 40 calcium, 12 carbon, and 48 oxygen, a composition which is represented by the formula $\text{CaO} \cdot \text{CO}_2$ or CaCO_3 ; but they are never formed by the direct union of dry carbon dioxide with a dry metallic oxide, the intervention of water being always required to bring about the combination. Potassium carbonate (pearlash) is the chief constituent of wood-ashes, sodium carbonate is contained in the ashes of marine plants, and is manufactured on a very large scale by heating sodium sulphate with lime and coal. These carbonates are soluble in water. The other metallic carbonates, which are insoluble, may be formed by mixing a solution of potassium or sodium carbonate with a soluble metallic salt; thus, when solutions of lead nitrate and sodium carbonate are mixed together, the lead and sodium change places, forming sodium nitrate, which remains dissolved, and lead carbonate, which, being insoluble in water, is precipitated in the form of a white powder: $\text{Pb}(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3 = 2\text{NaNO}_3 + \text{PbCO}_3$.

This is an example of *double decomposition*, the most frequent of all forms of chemical action.

The solution of carbon dioxide in water may be supposed to contain hydrogen carbonate or carbonic acid, consisting of 2 parts by weight of hydrogen, 12 carbon, and 48 oxygen, and represented by the formula H_2CO_3 or $\text{H}_2\text{O} \cdot \text{CO}_2$; but this compound is not known in the separate state, only in aqueous solutions.

Carbon Monoxide (commonly called *Carbonic Oxide*).—When carbon dioxide is passed over red-hot charcoal or metallic iron, one half of its oxygen is removed, and it becomes converted into carbon monoxide. A very good method of preparing this gas is to introduce into a flask fitted

with a bent tube some crystallized oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), and pour upon it five or six times as much strong oil of vitriol. On heating the mixture, the oxalic acid is resolved into water, carbon dioxide, and carbon monoxide, $\text{H}_2\text{C}_2\text{O}_4 = \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$; and by passing the gases through a strong solution of caustic potash, the first is withdrawn by absorption, while the second remains unchanged. Another and, it may be, preferable method, is to heat finely powdered yellow potassium ferrocyanide with eight or ten times its weight of concentrated sulphuric acid. The salt is entirely decomposed, yielding a most copious supply of perfectly pure carbon monoxide, which may be collected over water in the usual manner. The reaction is represented by the equation—



Carbon monoxide is a combustible gas, which burns with a beautiful pale-blue flame, generating carbon dioxide. It has never been liquefied. It is colorless, has very little odor, and is extremely poisonous—much more so than carbon dioxide. Mixed with oxygen, it explodes by the electric spark, but with some difficulty. Its specific gravity is 0.973; a litre weighs 1.2515 grams; 100 cubic inches weigh 30.21 grains.

The relation by volume of these oxides of carbon is as follows: Carbon dioxide contains its own volume of oxygen, that gas suffering no change of bulk by its conversion. One measure of carbon monoxide, mixed with half a measure of oxygen and exploded, yields one measure of carbon dioxide: hence carbon monoxide contains half its volume of oxygen.

Carbon monoxide unites with chlorine under the influence of light, forming a pungent, suffocating compound, possessing acid properties, called phosgene gas, or carbonyl chloride, COCl_2 . It is made by mixing equal volumes of carbon monoxide and chlorine, both perfectly dry, and exposing the mixture to sunshine: the gases unite quietly, the color disappears, and the volume becomes reduced to one-half. A more convenient method of preparing this gas consists in passing carbon monoxide through antimony pentachloride. It must be received over mercury, as it is decomposed by water. When pure it condenses to a liquid at 0° ; or more quickly at the temperature of a mixture of ice and salt.

Compounds of Carbon and Hydrogen.

The compounds of carbon and hydrogen already known are exceedingly numerous: perhaps all, in strictness, belong to the domain of organic chemistry, as they cannot, except in very few cases, be formed by the direct union of their elements, but always arise from the decomposition of a complex body of organic origin. It will be found convenient, notwithstanding, to describe three of them in this part of the volume, as they very well illustrate the important subjects of combustion and the nature of flame.

Methane or Marsh Gas; Light Carburetted Hydrogen; Fire-damp, CH_4 .

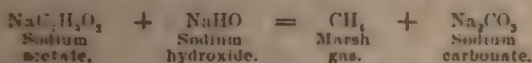
—This gas is but too often found to be abundantly disengaged in coal mines from the fresh-cut surface of the coal, and from remarkable apertures or "blowers," which emit for a great length of time a copious stream or jet of gas, probably existing in a state of compression, pent up in the coal.

When the mud at the bottom of pools in which water-plants grow is stirred, bubbles of gas escape, which may be easily collected. This, on

examination, is found to be chiefly a mixture of light carburetted hydrogen and carbon dioxide: the latter is easily absorbed by lime-water or caustic potash.

For a long time, no method was known by which methane could be produced in a state approaching to purity by artificial means: the various illuminating gases from pit-coal and oil, and that obtained by passing the vapor of alcohol through a red-hot tube, contain large quantities of it, associated, however, with other substances which hardly admit of separation; but Dumas has discovered a method by which it can be produced perfectly pure, and in any quantity.

A mixture is made of 40 parts crystallized sodium acetate, 40 parts solid sodium hydroxide, and 60 parts quicklime in powder. This mixture is transferred to a flask or retort, and strongly heated; the gas is disengaged in great abundance, and may be collected over water, while sodium carbonate remains behind. The reaction is represented by the equation—



The use of lime is merely to prevent the soda from fusing and attacking the flask.

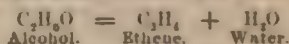
Methane is a colorless and nearly inodorous gas, which does not affect vegetable colors. It burns with a yellow flame, generating carbon dioxide and water. It is not poisonous, and may be respired to a great extent without apparent injury. The density of this compound is about 0.559, a litre weighing 0.71558 gram, and 100 cubic inches weighing 17.41 grains; it contains carbon and hydrogen associated in the proportion of 12 parts by weight of the former to 4 of the latter.

When 100 measures of this gas are mixed with 200 of pure oxygen in the eudiometer, and the mixture exploded by the electric spark, 100 measures of gas remain, which are entirely absorbable by a little solution of caustic potash. Now, carbon dioxide contains its own volume of oxygen; hence, one-half the oxygen added—that is, 100 measures—must have been consumed in uniting with the hydrogen. Consequently, the gas must contain twice its own measure of hydrogen, and enough carbon to produce, when completely burned, an equal quantity of carbon dioxide.

When chlorine is mixed with marsh-gas over water, no change follows, provided light be excluded. The presence of light, however, brings about decomposition, hydrochloric acid, carbon dioxide, and other products, being formed. It is important to remember that this gas is not acted upon by chlorine in the dark.

Ethene or Olefant Gas, C_2H_4 .—Strong spirit of wine is mixed with five or six times its weight of oil of vitriol in a glass flask, the tube of which passes into a wash-bottle containing caustic potash. A second wash-bottle, partly filled with oil of vitriol, is connected with the first, and furnished with a tube dipping into the water of the pneumatic trough. On the first application of heat to the contents of the flask, alcohol, and afterwards ether, make their appearance; but, as the temperature rises, and the mixture blackens, the ether-vapor diminishes in quantity, and its place becomes in great part supplied by a permanent inflammable gas; carbon dioxide and sulphurous oxide are also generated at the same time, forming traces of other products. The two last-mentioned gases are absorbed by the alkali in the first bottle, and the ether-vapor by the acid in the second, so that the olefant gas is delivered tolerably pure. The entire reaction is too complex to be discussed at the present moment; it will be

found fully described in the third part; but the ethene may be regarded as resulting from a simple dehydration of the alcohol by the oil of vitriol.



Olefiant gas thus produced is colorless, neutral, and but slightly soluble in water. Alcohol, ether, oil of turpentine, and even olive oil, dissolve it to a considerable extent. It has a faint odor of garlic. On the approach of a kindled taper it takes fire, and burns with a splendid white light, far surpassing in brilliancy that produced by marsh-gas. This gas, when mixed with oxygen and fired, explodes with extreme violence. Its density is 0.981; a litre weighs 1.25194 grams; 100 cubic inches weigh 30.57 grains.

By the use of the eudiometer, as already described, it has been found that each measure of ethene requires for complete combustion exactly three of oxygen, and produces under these circumstances two measures of carbon dioxide: whence it is evident that it contains twice its own volume of hydrogen combined with twice as much carbon as in methane.

By weight, these proportions are 24 parts carbon and 4 parts hydrogen.

Ethene is decomposed by passing it through a tube heated to bright redness; a deposit of charcoal and tar takes place, and the gas becomes converted into marsh-gas, or even into free hydrogen, if the temperature be very high. This latter change is, of course, attended by increase of volume.

Chlorine acts upon ethene in a very remarkable manner. When the two bodies are mixed, even in the dark, they combine in equal measures, and give rise to a heavy oily liquid, of sweetish taste and ethereal odor, to which the name of ethene chloride, or Dutch liquid, $\text{C}_2\text{H}_4\text{Cl}_2$, is given. It is from this peculiarity that the term *olefiant* gas is derived.

On mixing in a tall jar two measures of chlorine and one of ethene, and then quickly applying a light to the mouth of the vessel, the chlorine and hydrogen unite with flame, which passes quickly down the jar, while the whole of the carbon is set free in the form of a thick black smoke.

Ethine or Acetylene, C_2H_2 .—This hydrocarbon is formed by the direct union of its elements. Hydrogen and carbon do not combine at ordinary temperatures, or even under the influence of the most intense heat; but when an electric arc from a very powerful voltaic battery is passed between carbon poles in a current of hydrogen, the carbon and hydrogen unite to form acetylene. This compound is carried forward by the stream of hydrogen, and on passing the mixed gases into a solution of cuprous chloride, the acetylene is separated in the form of a red solid copper compound, which, when decomposed by hydrochloric acid, yields pure acetylene.

Acetylene is a colorless gas of specific gravity 0.92. It burns in the air with a bright smoky flame, and when mixed with chlorine, detonates almost instantly, even in diffused daylight, with separation of carbon.

Acetylene is one of the constituents of coal-gas, and is produced in the imperfect combustion of various bodies containing carbon and hydrogen. The modes of formation, reactions, and derivatives of this compound will be further considered under Organic Chemistry.

Coal Oil and Gases.—The manufacture of coal gas is a branch of industry of great interest and importance in several points of view. The process is one of great simplicity of principle, but requires, in practice, some delicacy in management to yield a good result.

When pit-coal is subjected to destructive distillation, a variety of products show themselves—permanent gases, steam and volatile oils, besides

and inconsiderable quantity of ammonia from the nitrogen always present in the coal. These substances vary very much in their proportions with the temperature at which the process is conducted, the permanent gases becoming more abundant with increased heat, but, at the same time, losing most of their value for the purposes of illumination.

The coal is distilled in cast-iron retorts, maintained at a bright-red heat, and the volatilized product is conducted into a long horizontal pipe of enormous dimensions, always half filled with liquid, into which the extremity of each separate tube dips: this is called the hydraulic main. The gas and its accompanying vapors are next made to traverse a refrigerator—usually a series of iron pipes, cooled on the outside by a stream of water; and the condensation of the tar and the ammoniacal liquid becomes complete, and the gas proceeds onwards to another part of the apparatus, in which it is deprived of the sulphuretted hydrogen and carbonic acid always present in the crude product. The separation was formerly effected by caustic lime, which readily absorbs the compounds in question. The use of lime, however, has been almost superseded by that of a mixture of saw-dust and iron oxide. This mixture, after having been used, is exposed for some time to the atmosphere, and is then fit for use a second time. The purifiers are large iron vessels filled either with slaked lime or with the saw-dust mixture. The gas is admitted at the bottom of the vessel, and made to pass over a large surface of the purifying agents. The last part of the operation, which, indeed, is often omitted, consists in passing the gas through dilute sulphuric acid, in order to remove ammonia. The quantity thus separated is very small, relatively, to the bulk of the gas, but in an extensive work, becomes an object of importance.

Coal-gas thus manufactured and purified is preserved for use in immense cylindrical receivers, closed at the top, suspended in tanks of water by chains, in which counterpoises are attached, so that the gas-holders rise and sink with the liquid as they become filled from the purifiers or emptied by the mains. These latter are made of large diameter, to diminish as much as possible the resistance experienced by the gas in passing through such a length of pipe. The joints of these mains are still made in so imperfect a manner that immense loss is experienced by leakage when pressure upon the gas exceeds that exerted by a column of water an inch in height.*

Coal gas varies very much in composition, judging from its variable density and illuminating powers, and from the analyses which have been made. The difficulties of such investigations are very great, and unless particular precaution be taken, the results are merely approximate. The purified gas is believed to contain the following substances, of which the first is the most abundant and the second the most valuable:—

- Methane, or Marsh gas.
- Ethene, or Olefiant gas.
- Ethine, or Acetylene.
- Hydrogen.

* It may give some idea of the extent of this species of manufacture, to mention that in the year 1833, for lighting London and the suburbs alone, there were seventeen public gas works, and £2,500,000 invested in pipes and apparatus. The yearly revenue amounted to £10,000, and the consumption of coal in the same period to 180,000 tons, 100 millions of cubic feet of gas being made in the year. There were 14,000 private lights, and 35,000 street lamps. 800 tons of coals were used in the retorts in the space of twenty-four hours at midwinter; and 1,120,000 cubic feet of gas consumed in the longest night.—*Ure, Dictionary of Arts and Manufactures.*

Since that time, the production of gas has been enormously increased. The amount of coal used in London for gas-making in the year ending June, 1852, is estimated at 400,000 tons, which on an average would yield about 4000 millions of cubic feet of gas. In the year 1857 the mains in the London streets had reached the extraordinary length of 2000 miles.

Carbon Monoxide.

Nitrogen.

Vapors of volatile liquid Hydrocarbons.*

Vapor of Carbon Bisulphide.

Separated by Condensation and by the Purifiers.

Tar and Volatile Oils.

Ammonium Sulphate, Chloride, and Sulphide.

Hydrogen Sulphide.

Carbon Dioxide.

Hydrocyanic acid, or Ammonium Cyanide.

Sulphocyanic acid, or Ammonium Sulphocyanate.

A far better illuminating gas may be prepared from oil, by dropping it into a red-hot iron retort filled with coke; the liquid is in great part decomposed and converted into permanent gas, which requires no purification, as it is quite free from the ammoniacal and sulphur compounds which vitiate gas from coal. Many years ago this gas was prepared in London; it was compressed, for the use of the consumer, into strong iron vessels, to the extent of thirty atmospheres; these were furnished with a screw-valve of peculiar construction, and exchanged for others when exhausted. The comparatively high price of the material, and other circumstances, led to the abandonment of the undertaking. On the Continent gas is now extensively prepared from wood.

Combustion, and the Structure of Flame.

When any solid substance capable of bearing the fire is heated to a certain point, it emits light, the character of which depends upon the temperature. Thus, a bar of platinum or a piece of porcelain, raised to a particular temperature, becomes what is called red-hot, or emissive of red light. At a higher degree of heat, this light becomes whiter and more intense, and when urged to the utmost, as in the case of a piece of lime placed in the flame of the oxyhydrogen blow-pipe, the light becomes exceedingly powerful, and acquires a tint of violet. Bodies in these states are said to be *incandescent* or *ignited*.

Again, if the same experiment be made on a piece of charcoal, similar effects will be observed; but something in addition; for whereas the platinum and porcelain, when removed from the fire, or the lime from the blow-pipe flame, begin immediately to cool, and emit less and less light, until they become completely obscure, the charcoal maintains to a great extent its high temperature. Unlike the other bodies, too, which suffer no change whatever, either of weight or substance, the charcoal gradually wastes away until it disappears. This is what is called *combustion*, in contradistinction to mere ignition; the charcoal burns, and its temperature is kept up by the heat evolved in the act of union with the oxygen of the air.

In the most general sense, a body in a state of combustion is one in the act of undergoing intense chemical action; any chemical action whatsoever, if its energy rise sufficiently high, may produce the phenomenon of combustion, by heating the body to such an extent that it becomes luminous.

In all ordinary cases of combustion, the action lies between the burning body and the oxygen of the air; and since the materials employed for the economical production of heat and light consist of carbon chiefly, or that substance conjoined with a certain proportion of hydrogen and oxygen, all

* These bodies increase the illuminating power, and confer on the gas its peculiar odor.

common effects of this nature are cases of the rapid and violent oxidation of carbon and hydrogen by the aid of the free oxygen of the air. The heat must be referred to the act of chemical union, and the light to the elevated temperature.

By this principle, it is easy to understand the means which must be adopted to increase the heat of ordinary fires to the point necessary to melt refractory metals, and to bring about certain desired effects of chemical decomposition. If the rate of consumption of the fuel can be increased by a more rapid introduction of air into the burning mass, the intensity of the heat will of necessity rise in the same ratio, the quantity of heat evolved being fixed and definite for the same constant quantity of chemical action. This increased supply of air may be effected by two distinct methods: it may be forced into the fire by bellows or blowing-machines, as in the common forge and in the blast and cupola-furnaces of the iron-worker; or it may be drawn through the burning materials by the help of a tall chimney, the fireplace being closed on all sides, and no entrance of air allowed, save between the bars of the grate. Such is the kind of furnace generally employed by the scientific chemist in assaying and in the reduction of metallic oxides by charcoal: the principle will be at once understood by the aid of the sectional drawing (fig. 109), in which a crucible is represented arranged in the fire for an operation of the kind mentioned.

The "reverberatory" furnace (fig. 110) is one very much used in the arts when substances are to be exposed to heat without contact with the fuel.

Fig. 109.

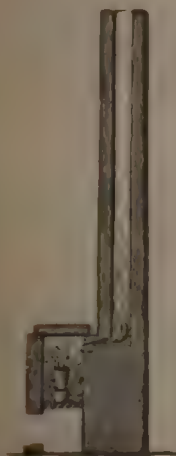


Fig. 110.



The fire-chamber is separated from the bed or hearth of the furnace by a low wall or bridge of brickwork, and the flame and heated air are reflected downwards by the arched form of the roof. Any degree of heat can be obtained in a furnace of this kind—from the temperature of dull redness to that required to melt very large quantities of cast-iron. The fire is urged by a chimney provided with a sliding-plate, or damper, to regulate the draught.

Solids and liquids, as melted metal, possess, when sufficiently heated, the faculty of emitting light: the same power is exhibited by gaseous bodies, but the temperature required to render a gas luminous is incomparably higher than in the cases already described. Gas or vapor in this condition constitutes *flame*, the actual temperature of which generally exceeds that of the white heat of solid bodies.

The light emitted from pure flame is often exceedingly feeble: but the illuminating power may be immensely increased by the presence of solid matter. The flame of hydrogen, or of the mixed gases, is scarcely visible in full daylight; in a dusty atmosphere, however, it becomes much more luminous by igniting to intense whiteness the floating particles with which it comes in contact. The piece of lime in the blow-pipe flame cannot have a higher temperature than that of the flame itself, yet the light it throws off is infinitely greater.

On the other hand, it is possible, as recently pointed out by Dr. Frankland, to produce very bright flames in which no solid particles are present. Metallic arsenic burnt in a stream of oxygen produces an intense white flame, although both the metal itself and the product of its combustion (arsenious oxide) are gaseous at the temperature of the flame. The combustion of a mixture of nitrogen dioxide and carbon bisulphide also produces a dazzling white flame, without any separation of solid matter.

The conditions most essential to luminosity in a flame are a high temperature, and the presence of gases or vapors of considerable density. The effect of high temperature is seen in the greater brightness of the flame of sulphur, phosphorus, and, indeed, all substances, when burnt in pure oxygen, as compared with that which results from their combustion in common air; in the former case, the whole of the substances present take part in the combustion, and generate heat, whereas, in the latter, the temperature is lowered by the presence of a large quantity of nitrogen, which contributes nothing to the effect. The relation between the luminosity of a flame and the vapor-densities of its constituents may be seen from the following table, in which the vapor-densities are referred to that of hydrogen as unity.

Relative Densities of Gases and Vapors.

| | | | | | | | | | |
|-------------------|---|---|---|---|-----|--------------------|---|--------|-----|
| Hydrogen | . | . | . | . | 1 | Arsenious chloride | . | . | 90½ |
| Water | . | . | . | . | 9 | Phosphoric oxide | . | 71, or | 142 |
| Hydrochloric acid | . | . | . | . | 18½ | Metallic arsenic | . | . | 150 |
| Carbon dioxide | . | . | . | . | 22 | Arsenious oxide | . | . | 198 |
| Sulphur dioxide | . | . | . | . | 32 | | | | |

A comparison of these numbers shows that the brightest flames are those which contain the densest vapors. Hydrogen burning in chlorine produces a vapor more than twice as heavy as that resulting from its combustion in oxygen, and accordingly the light produced in the former case is stronger than in the latter; carbon and sulphur burning in oxygen produce vapors of still greater density, namely, carbon dioxide and sulphur dioxide, and their combustion gives a still brighter light; lastly, phosphorus, which has a very dense vapor, and likewise yields a product of great vapor-density, burns in oxygen with a brilliancy which the eye can scarcely endure. Moreover, the luminosity of a flame is increased by condensing the surrounding gaseous atmosphere, and diminished by rarefying it. The flame of arsenic burning in oxygen may be rendered quite feeble by rarefying the oxygen; and, on the contrary, the faint flame of an ordinary spirit-lamp becomes very bright when placed under the receiver of a condensing-pump. Frankland has also found that candles give much less light when burning on the top of Mont Blanc than in the valley below, although the

of combustion in the two cases is nearly the same. The effect of condensation in increasing the brightness of a flame is also strikingly seen in the combustion of a mixture of oxygen and hydrogen, which gives a feeble light when burnt under the ordinary atmospheric pressure, as in the oxy-hydrogen blow-pipe, but a very bright flash when exploded in an eudiometer (p. 138), in which the water-vapor produced by the combustion is prevented from expanding.

Fig. 111.



Flames burning in the air, and not supplied with oxygen from another source, are, as already stated, hollow, the combustion being necessarily confined to the spot where the bodies unite. That of a lamp or candle when carefully used, is seen to consist of three separate portions. The central part, easily rendered evident by depressing upon it a piece of fine wire-gauze, consists of combustible matter drawn up by the capillarity of the wick, and volatilized by heat. This is surrounded by a highly luminous cone or envelope, which, in contact with a cold body, deposits soot. Outside, a second cone is to be traced, feeble in its lighting power, but having an exceedingly high temperature. The most probable explanation of these appearances is as follows: Carbon and hydrogen are very unequal in their attraction for oxygen, the latter greatly exceeding the former in this respect; consequently, when both are present, and the supply of oxygen is limited, hydrogen takes up the greater portion of the oxygen, leaving the exclusion of a great part of the carbon.

Fig. 112.



This happens, in the case under consideration, at a little distance within the outer surface of the flame, namely, in the luminous portion; the little portion which has penetrated thus far inwards is consumed by the hydrogen, and hydro-carbons separated, rich in carbon and of great density in the state of vapor (naphthalene, chrysene, pyrene, &c.).

These hydro-carbons, which would form smoke if they were cooler, and are deposited on a cold body in the flame in the form of soot,* become intensely white by the burning hydrogen, and evolve a light whose whiteness marks a very elevated temperature. Outside this and scarcely visible cone, these hydro-carbons undergo combustion.

Coal-gas exhibits the same phenomena; but, if it has been previously mingled with air, or if air be freely mixed with, or driven into, the flame, no such action of carbon occurs; the hydrogen and carbon are carried together, forming vapors of much lower density, and the illuminating power almost disappears.

A common mouth blow-pipe is an instrument of great utility; it is merely a brass tube fitted with an air-tight mouth-piece and terminated by a jet having a small aperture, by which a current of air is driven into the flame of a candle. The best form is perhaps that contrived by Mr. Pepys, and shown in fig. 112.

The flame so produced is very peculiar.

In the case of the double envelope just described, two long pointed cones are observed (fig. 113), which, when the blow-pipe is good, and the aper-

* Soot is not pure carbon, but a mixture of heavy hydro-carbons.

ture smooth and round, are very well defined, the outer cone being yellowish, and the inner blue. A double combustion is, in fact, going on, by

Fig. 113.



the blast in the inside, and by the external air. The space between the inner and outer cones is filled with exceedingly hot combustible matter, possessing strong reducing or deoxidizing powers; while the highly heated air just beyond the point of the exterior cone oxidizes with great facility. A small portion of matter, supported on a piece of charcoal, or fixed in a ring at the end of a fine platinum wire, can thus in an instant be exposed to a very high degree of heat under these contrasted circumstances, and observations of great value made in a very short

time. The use of the instrument requires an even and uninterrupted blast of some duration, by a method easily acquired with a little patience: it consists in employing for the purpose the muscles of the cheeks alone, respiration being conducted through the nostrils, and the mouth from time to time replenished with air, without intermission of the blast.

The Argand lamp, adapted to burn either oil or spirit, but especially the latter, is a very useful piece of chemical apparatus. In this lamp the wick is cylindrical, the flame being supplied with air both inside and outside: the combustion is greatly aided by the chimney, which is made of copper when the lamp is used as a source of heat.

Fig. 114 exhibits, in section, an excellent lamp of this kind for burning

Fig. 114.

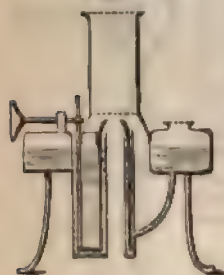


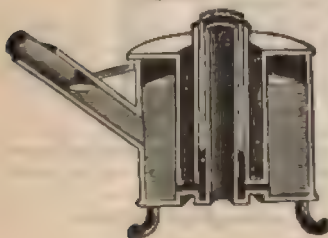
Fig. 115.



alcohol or wood-spirit. It is constructed of thin copper, and furnished with ground caps to the wick-holder and aperture,* by which the spirit is introduced, in order to prevent loss when the lamp is not in use. Glass spirit-lamps (fig. 115), fitted with caps to prevent evaporation, are very convenient for occasional use, being always ready and in order.†

* When in use, this aperture must always be open, otherwise an accident is sure to happen; the heat expands the air in the lamp, and the spirit is forced out in a state of inflammation.

Fig. 116.



† The spirit-lamp represented in fig. 116, is one contrived by Dr. J. K. Mitchell. "It is made of tinned iron. The alcohol is poured out by means of the hollow handle, and is admitted to the cylindrical burner by two or three tubes which are placed at the very bottom of the fountain. By such an arrangement of parts, the alcohol may be added as it is consumed, and the flame kept uniform; and as the pipes which pass to the burner are so remote from the flame, the alcohol never becomes heated so as to fly off through the vent-hole, and thus to cause greater waste and danger of explosion."

A cylindrical chimney is an advantageous addition for many purposes. It may be made of tin-plate or copper.—R. B.

In London, and other large towns where coal-gas is to be had, it is constantly used with the greatest economy and advantage in every respect as a source of heat. Retorts, flasks, capsules, and other vessels, can be thus exposed to an easily regulated and invariable temperature for many successive hours. Small platinum crucibles may be ignited to redness by placing them over the flame on a little wire triangle. The arrangement shown in fig. 117, consisting of a common Argand gas-burner fixed on a heavy and low foot, and connected with a flexible tube of caoutchouc or other material, is very convenient.



Fig. 117.

A higher temperature, and a perfectly smokeless flame, are, however, obtained by burning the gas previously mixed with air. Such a flame is easily produced by placing a cap of wire-gauze on the chimney of the Argand burner just described, and setting fire to the gas above the wire-gauze. The flame does not penetrate below, but the gas, in passing up the chimney, becomes mixed with air, and this mixture burns above the cap with a blue, smokeless flame.

Another kind of burner for producing a smokeless flame has been contrived by Professor Bunsen, and is now very generally used in chemical laboratories. In this burner (fig. 118) the gas, supplied by a flexible tube *a*, passes through a set of small holes into the box *b*, in which it mixes with atmospheric air entering freely by a number of holes near the top of the box. The gaseous mixture passes up the tube *c*, and is inflamed at the top, where it burns with a tall, blue, smokeless flame, giving very little light, but much heat. By arranging two or more such tubes, together with an air-box containing a sufficient number of holes, a very powerful burner may be constructed.

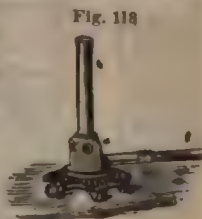


Fig. 118.

Considerable improvements in this form of burner have been made by Mr. Griffin, who has also constructed, on the same principle, powerful gas-furnaces, affording heat sufficient for the decomposition of silicates, and the fusion of considerable quantities of copper or iron.* The principle of burning a mixture of gas and air is also applied in Hofmann's gas-furnace for organic analysis, which will be described under Organic Chemistry.

The kindling-point, or temperature at which combustion commences, is very different with different substances; phosphorus will sometimes take fire in the hand; sulphur requires a temperature exceeding that of boiling water; charcoal must be heated to redness. Among gaseous bodies the same fact is observed: hydrogen is inflamed by a red-hot wire; light carburetted hydrogen requires a white heat to effect the same thing. When flame is cooled by any means below the temperature at which the rapid oxidation of the combustible gas occurs, it is at once extinguished. Upon this depends the principle of Sir H. Davy's invaluable safety-lamp.

Mention has already been made of the frequent disengagement of great quantities of light carburetted hydrogen gas in coal mines. This gas, mixed with seven or eight times its volume of atmospheric air, becomes highly explosive, taking fire at a light and burning with a pale-blue flame; and many fearful accidents have occurred from the ignition of large quan-

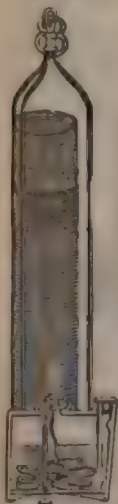
* See the article on Gas-burners and Furnaces in Watts's Dictionary of Chemistry, II. 762.

tities of mixed gas and air occupying the extensive galleries and workings of a mine. Davy undertook an investigation with a view to discover some remedy for this constantly occurring calamity; his labors resulted in some exceedingly important discoveries respecting flame, which led to the construction of the lamp which bears his name.

When two vessels filled with a gaseous explosive mixture are connected by a narrow tube, and the contents of one fired by the electric spark, or otherwise, the flame is not communicated to the other, provided the diameter of the tube, its length, and the conducting power for heat of its material, bear a certain proportion to each other; the flame is extinguished by cooling, and its transmission rendered impossible.

In this experiment, high conducting power and diminished diameter compensate for diminution in length; and to such an extent can this be carried, that metallic gauze, which may be looked upon as a series of very short square tubes arranged side by side, when of sufficient degree of fineness, arrests in the most complete manner the passage of flame in explosive mixtures. Now the fire-damp mixture has an exceedingly high kindling point;

Fig. 119.



a red heat does not cause inflammation; consequently, the gauze will be safe for this substance, when flame would pass in almost any other case.

The miner's safety-lamp is merely an ordinary oil-lamp, the flame of which is inclosed in a cage of wire-gauze, made double at the upper part, containing about 400 apertures to the square inch. The tube for supplying oil to the reservoir reaches nearly to the bottom of the latter, while the wick admits of being trimmed by a bent wire passing with friction through a small tube in the body of the lamp; the flame can thus be kept burning for any length of time, without the necessity of unscrewing the cage. When this lamp is taken into an explosive atmosphere, although the fire-damp may burn within the cage with such energy as sometimes to heat the metallic tissue to dull redness, the flame is not communicated to the mixture on the outside.

These effects may be conveniently studied by suspending the lamp in a large glass jar, and gradually admitting coal-gas below. The oil-flame is at first elongated, and then, as the proportion of gas increases, extinguished, while the interior of the gauze cylinder becomes filled with the burning mixture of gas and air. As the atmosphere becomes purer, the wick is once more relighted. These appearances are so remarkable that the lamp becomes an admirable indicator of the state of the air in different parts of the mine.*

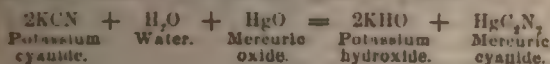
The same principle is ingeniously applied in the construction of Hemi-ming's oxyhydrogen safety-jet already mentioned. This is a tube of brass about four inches long, filled with straight pieces of fine brass wire, the whole being tightly wedged together by a pointed rod, forcibly driven into the centre of the bundle. The arrangement thus presents a series

* This is the true use of the lamp, namely, to permit the viewer or superintendent, without risk to himself, to examine the state of the air in every part of the mine, and to enable workmen to continue their labors in an atmosphere habitually explosive, which must be unfit for human respiration, although the evil effects may be slow to appear. Owners of coal-mines should be compelled either to adopt efficient means of ventilation, or to close workings of this dangerous character altogether.

of metallic tubes, very long in proportion to their diameter, the cooling powers of which are so great as to prevent the possibility of the passage of flame, even with oxygen and hydrogen. The jet may be used, as before mentioned, with a common bladder, without the chance of explosion. The fundamental fact of flame being extinguished by contact with a cold body, may be strikingly shown by twisting a copper wire into a short spiral, about 0.1 in. in diameter, and then passing it *cold* over the flame of a wax candle; the latter is extinguished. If the spiral be now heated to redness by a spirit lamp, and the experiment repeated, no such effect follows.

Compound of Carbon and Nitrogen. Cyanogen.

When a stream of air is passed over a mixture of charcoal and potassium carbonate kept at a bright red heat, the nitrogen of the air unites with the carbon and the potassium, forming a compound called potassium cyanide, containing 39 parts of potassium, 12 of carbon, and 14 of nitrogen, and represented by the formula KCN . It is a crystalline salt, which dissolves easily in water, and decomposes mercuric oxide, forming potassium hydrate and mercuric cyanide:—



Now, when dry mercuric cyanide, which is a white crystalline substance, is strongly heated in a glass tube, fitted up like that used for the evolution of oxygen from mercuric oxide (p. 121), it splits up, like the oxide, into metallic mercury, and a gaseous body called cyanogen, containing 12 parts by weight of carbon and 14 of nitrogen, and represented by the formula CN . It must be collected over mercury, as it is rapidly absorbed by water.

Cyanogen is a colorless gas, having a pungent and very peculiar odor, remotely resembling that of peach-kernels. Exposed while at the temperature of $7.2^\circ C.$ ($45^\circ F.$) to a pressure of 3.6 atmospheres, it condenses to a thin, colorless, transparent liquid. It is inflammable, and burns with a beautiful purple or peach-blossom-colored flame, generating carbon dioxide and liberating nitrogen. Its specific gravity is 1.801 referred to air, or 26 referred to hydrogen as unity. One volume of it exploded with 2 vols. oxygen yields 1 vol. nitrogen and 2 vols. carbon dioxide. Now, the weights of equal volumes of cyanogen, nitrogen, and carbon dioxide are as 26 : 14 : 22. Consequently, 26 parts by weight of cyanogen yield by combustion 14 parts of nitrogen and 44 parts of carbon dioxide, containing 12 parts of carbon; or $26 \text{ cyanogen} = 12 \text{ carbon} + 14 \text{ nitrogen}$.

Water dissolves 4 or 5 times its volume of cyanogen gas, and alcohol a much larger quantity: the solution rapidly decomposes, yielding ammonium oxalate, a brown insoluble matter, and other products.

Cyanogen unites (though not directly) with hydrogen, forming the very poisonous compound called hydrocyanic or prussic acid; and with metals, forming compounds called cyanides, analogous in composition and character to the chlorides, iodides, bromides, etc. In short, this group of elements, represented by the formula CN , combines with elementary bodies, and is capable of passing from one state of combination to another, just as if it were itself an elementary body. Such a group of elements is called a compound *radicle*. We have already had occasion to notice

Fig. 120.



another such group, viz., ammonium, NH_4 . Cyanogen, however, is analogous in its chemical relations to the non-metallic elements, chlorine, bromine, oxygen, etc.; whereas ammonium is a quasi-metal analogous to potassium, etc.

The compounds of cyanogen will be further considered under Organic Chemistry.

CHLORINE.

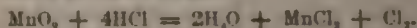
Atomic weight, 35.5. Symbol, Cl.

This substance is a member of a very important natural group, containing also iodine, bromine, and fluorine. So great a degree of resemblance exists between these bodies in all their chemical relations, especially between chlorine, bromine, and iodine, that the history of one will almost serve, with a few little alterations, for that of the rest. On account of the occurrence of chlorine, bromine, and iodine in sea-water, the elements of this group are called halogen-elements, and their metallic compounds, haloid compounds.*

Chlorine is a very abundant substance: in common salt it exists in combination with sodium. It is most easily prepared by pouring strong hydrochloric acid upon finely powdered black oxide of manganese (MnO_2) contained in a retort or flask (fig. 121), and applying a gentle heat; a heavy yellow gas is disengaged, which is the substance in question.

It may be collected over warm water, or by displacement: the mercurial trough cannot be employed, as the chlorine rapidly acts upon the metal, and becomes absorbed.

The reaction consists in an interchange between the 2 atoms of oxygen of the manganese dioxide and 4 atoms of chlorine from the hydrochloric acid, the oxygen uniting with the hydrogen to form water, while, of the chlorine, one-half unites with the manganese, forming a chloride, MnCl_2 , and the other half is given off as gas:—



The same process is used for the preparation of chlorine on the manufacturing scale, the hydrochloric acid which is evolved in large quantities by heating common salt with sulphuric acid, in Leblanc's soda-process, being utilized for the purpose.

The waste-liquor obtained in the chlorine manufacture consists of an impure solution of manganous chloride, MnCl_2 , from which the manganese may be separated by an alkali in the form of manganous oxide, MnO . But to render the manganese thus precipitated again available for the production of chlorine, it must first be brought to the state of dioxide, and this may be effected by mixing the manganese liquor with an excess of hot milk of lime, or magnesia, and blowing hot air through the mixture. By this means, a compound of manganese dioxide with lime or magnesia, e.g., CaO.MnO_2 , or CaMnO_3 , called calcium or magnesium manganite, is formed, which, when heated with hydrochloric acid, gives off chlorine in the manner above described. This is Weldon's process for the regeneration of manganese, which is now largely used both in England and on the Continent.

From 42c, the sea.

A process for the separation of chlorine from hydrochloric acid, without the use of any manganese compound, has been introduced by Mr. H. Deacon. It consists in passing a mixture of hydrochloric acid gas and oxygen, or air, over cupric sulphate or other cupric salt heated to $370-400^{\circ}\text{C}$. ($698-752^{\circ}\text{F}$.), the hydrochloric acid being then decomposed, its hydrogen combining with the oxygen, and the chlorine being set free. The best way of conducting the process is to pass the mixed gases over pieces of brick soaked in solution of cupric sulphate and dried. The action of the copper salt is not well understood, but appears to belong to that class of phenomena called catalytic or contact actions. Other metallic salts act in a similar way, but less completely.

Chlorine is a yellow gaseous body, of intolerably suffocating properties, producing very violent cough and irritation when inhaled, even in exceedingly small quantity. It is soluble to a considerable extent in water, that liquid absorbing at 15.5° about twice its volume, and acquiring the color and odor of the gas. When this solution is exposed to light, it is slowly changed, by decomposition of water, into hydrochloric acid, the oxygen being at the same time liberated. When moist chlorine gas is exposed to a cold of 0° , yellow crystals are formed, which consist of a definite compound of chlorine and water containing 35.5 parts of the former to 90 of the latter.

Chlorine has a specific gravity of 2.47; a litre of it weighs 3.17344 grams; exposed to a pressure of about four atmospheres, it condenses to a yellow limpid liquid.

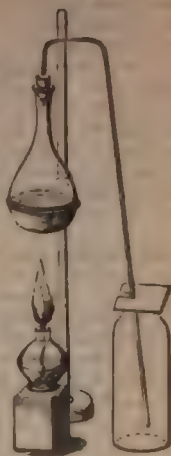
Chlorine has but little attraction for oxygen, its energies being principally exerted towards hydrogen and the metals. A lighted taper plunged into the gas continues to burn with a dull-red light, and emits a large quantity of smoke, the hydrogen of the wax being alone consumed, and the carbon separated. If a piece of paper be wetted with oil of turpentine, and thrust into a bottle filled with chlorine, the chemical action of the latter upon the hydrogen is so violent as to cause inflammation, accompanied by a copious deposit of soot. Chlorine may, by indirect means, be made to combine with carbon; but this combination never occurs under the circumstances described.

Phosphorus takes fire spontaneously in chlorine, burning with a pale and feebly luminous flame. Several of the metals, as copper-leaf, powdered antimony, and arsenic, undergo combustion in the same manner. A mixture of equal measures of chlorine and hydrogen explodes with violence on the passage of an electric spark, or on the application of a lighted taper, hydrochloric acid gas being formed. Such a mixture may be kept in the dark for any length of time without change: exposed to diffuse daylight, the two gases slowly unite, while the direct rays of the sun induce instantaneous explosion.

The most characteristic property of chlorine is its bleaching power; the most stable organic coloring principles are instantly decomposed and destroyed by this remarkable agent: indigo, for example, which resists the action of strong oil of vitriol, is converted by chlorine into a brownish substance, to which the blue color cannot be restored. The presence of water is essential to these changes, for the gas in a state of perfect dryness is incapable even of affecting litmus.

Chlorine is largely used in the arts for bleaching linen and cotton goods,

Fig. 121.



rag for the manufacture of paper, etc. For these purposes, it is employed, sometimes in the state of gas, sometimes in that of solution in water, but more frequently in combination with lime, forming the substance called bleaching-powder. It is also one of the best and most potent substances that can be used for the purpose of disinfection, but its employment requires care. Bleaching-powder mixed with water, and exposed to the air in shallow vessels, becomes slowly decomposed by the carbonic acid of the atmosphere, and the chlorine is evolved: if a more rapid disengagement be wished, a little acid of any kind may be added. In the absence of bleaching-powder, either of the methods for the production of the gas described may be had recourse to, always taking care to avoid an excess of acid.

Hydrogen Chloride, or Hydrochloric Acid, HCl; also called *Chlorhydric* and *Muriatic Acid*.—This substance, in a state of solution in water, has long been known. The gas is prepared with the utmost ease by heating, in a flask fitted with a cork and bent tube, a mixture of common salt and oil of vitriol diluted with a small quantity of water; it must be collected by displacement, or over mercury. It is a colorless gas, which fumes strongly in the air from condensing the atmospheric moisture; it has an acid, suffocating odor, but is much less offensive than chlorine. Exposed to a pressure of 40 atmospheres, it liquefies.

Hydrochloric acid gas has a density of 1.269 compared with air, or 18.25 compared with hydrogen as unity. It is exceedingly soluble in water, that liquid taking up, at the temperature of the air, about 418 times its bulk. The gas and solution are powerfully acid.

The action of sulphuric acid on common salt, or any analogous substance, is explained by the equation,



The composition of hydrochloric acid may be determined by synthesis: when a measure of chlorine and a measure of hydrogen are fired by the electric spark, two measures of hydrochloric acid gas result, the combination being unattended by change of volume. By weight it contains 35.5 parts of chlorine and 1 part of hydrogen.

Solution of hydrochloric acid, the liquid acid of commerce, is a very important preparation, and of extensive use in chemical pursuits: it is best prepared by the following arrangement:—

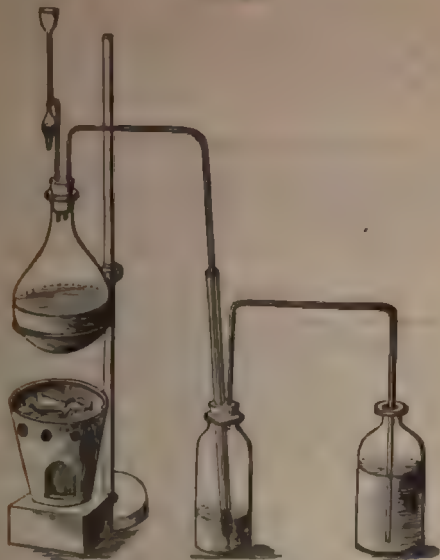
A large glass flask, containing a quantity of common salt, is fitted with a cork and bent tube, in the manner represented in fig. 122; this tube passes through and below a second tube into a wide-necked bottle, containing a little water, into which the open tube dips. A bent tube is adapted to another hole in the cork of the wash-bottle, so as to convey the purified gas into a quantity of distilled water, by which it is instantly absorbed: the joints are made air-tight by melting a little yellow wax over the corks.

A quantity of sulphuric acid, about equal in weight to the salt, is then slowly introduced by the funnel: the disengaged gas is at first wholly absorbed by the water in the wash-bottle, but when this becomes saturated, it passes into the second vessel, and there dissolves. When all the acid has been added, heat may be applied to the flask by a charcoal chauffer, until its contents appear nearly dry, and the evolution of gas almost ceases, when the process may be stopped. As much heat is given out during the condensation of the gas, it is necessary to surround the condensing vessel with cold water.

The simple wash-bottle, shown in figure 122, will be found an exceedingly useful contrivance in a great number of chemical operations. It

water in the present, and in many similar cases to retain any liquid or solid matter mechanically carried over with the gas, and it may be always

Fig. 122.



employed when a gas of any kind is to be passed through an alkaline or other solution. The open tube dipping into the liquid prevents the creation of a partial vacuum by absorption, and the liquid of the second vessel from being driven into the first.

Fig. 123.

The arrangement by which the acid is introduced also deserves a moment's notice (fig. 123). The tube is bent twice upon itself, and a bulb blown in one portion: the liquid poured into the funnel rises upon the opposite side of the first bend until it reaches the second, it then flows over and runs into the flask. Any quantity can then be got into the latter without the introduction of air, and without the escape of gas from the interior. The funnel acts also as a kind of safety-valve, and in both directions; for if by any chance the delivery-tube should be stopped, and the issue of gas prevented, its increased elastic force soon drives the little column of liquid out of the tube, the gas escapes, and the vessel is saved. On the other hand, any absorption within is quickly compensated by the entrance of air through the liquid in the bulb.



The plan employed on the large scale by the manufacturer is the same in principle as that described; he merely substitutes a large iron cylinder, or apparatus made of lead, for the flask, and vessels of stoneware for those of glass.

Pure solution of hydrochloric acid is transparent and colorless: when strong it fumes in the air by evolving a little gas. It leaves no residue on

evaporation, and gives no precipitate or opacity with diluted solution of barium chloride. When saturated with the gas, it has a specific gravity of 1.21, and contains about 42 per cent. of real acid. The commercial acid which is obtained in immense quantity as a secondary product in the manufacture of sodium sulphate by the action of sulphuric acid upon common salt, has usually a yellow color, and is very impure, containing salts, sulphuric acid, chloride of iron, and organic matter. It may be rendered sufficiently pure for most purposes by diluting it to the density of 1.1, which happens when the strong acid is mixed with its own bulk, or rather less, of water, and then distilling it in a retort furnished with a Liebig's condenser.

On distilling an aqueous solution of hydrochloric acid, an acid is produced, boiling at 110°C . (230°F .), which contains 20.22 per cent. of anhydrous hydrochloric acid: a more concentrated solution, when heated, gives off hydrochloric acid gas; a weaker solution loses water. Rosecoe and Dittmar have proved that the composition of the distillate varies with the atmospheric pressure; it cannot, therefore, be viewed as a chemical compound.

A crystalline hydrate of hydrochloric acid, having the composition $\text{HCl} \cdot 2\text{H}_2\text{O}$, is formed by passing a stream of nearly dry hydrochloric acid gas through the concentrated aqueous acid cooled by a freezing mixture to -22°C . (-7.6°F .). The crystals decompose rapidly in the air, emitting white fumes; they dissolve very quickly in water at ordinary temperatures; very slowly at -18°C . (-0.4°F .).

Mixtures of snow and hydrochloric acid form very powerful and economical refrigerants. With two parts of snow and 1 part of the acid a lowering of temperature to -32°C . (-25.6°F .) is readily obtained.*

Nitro-hydrochloric Acid.—A mixture of nitric and hydrochloric acid has long been known under the name of *aqua regia*, from its property of dissolving gold. When these two substances are heated together, they both undergo decomposition, nitrogen tetroxide and chlorine being evolved. This, at least, appears to be the final result of the action: at a certain stage, however, two peculiar substances, consisting of nitrogen, oxygen, and chlorine (chloronitric acid gas, NOCl_2 , and chloronitrous gas, NOCl), appear to be formed. It is only the chlorine which attacks the metal.

The presence of hydrochloric acid, or any other soluble chloride, is easily detected by solution of silver nitrate. A white curdy precipitate is produced, insoluble in nitric acid, freely soluble in ammonia, and subject to blacken by exposure to the light.

Oxides and Oxyacids of Chlorine.

There are four oxyacids of chlorine, which may be regarded as oxides of hydrochloric acid: thus—

| | Formula. | Composition by weight | | | |
|--------------------|-----------------|-----------------------|---|-----------|---------|
| | | Hydrogen. | | Chlorine. | Oxygen. |
| Hydrochloric acid, | HCl | 1 | + | 35.5 | |
| Hypochlorous acid, | HClO | 1 | + | 35.5 | 16 |
| Chlorous acid, | HClO_2 | 1 | + | 35.5 | 32 |
| Chloric acid, | HClO_3 | 1 | + | 35.5 | 48 |
| Perchloric acid, | HClO_4 | 1 | + | 35.5 | 64 |

The anhydrous chlorine oxides corresponding with hypochlorous and chlorous acids are also known, namely—

* *Pierre and Puchot, Comptes rendus, lxxiii. 13.*

| | Chlorine. | | Chlorine. | | Oxygen. |
|---|-----------|---|-----------|---|---------|
| Chlorine monoxide, or Hypochlorous oxide, Cl_2O | 35.5 | + | 35.5 | + | 16 |
| Chlorine trioxide, or Chlorous oxide, Cl_2O_3 | 35.5 | + | 35.5 | + | 48 |

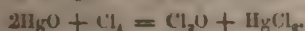
Also, an oxide to which there is no corresponding acid, namely—

| | Chlorine. | | Oxygen. |
|---|-----------------|---|---------|
| Chlorine tetroxide, Cl_2O_4 | 2×35.5 | + | 64 |

The oxides corresponding with chloric and perchloric acid have not been obtained.

Hypochlorous and chloric acids are produced by the action of chlorine on certain metallic oxides in presence of water; hypochlorous and chlorous acids also by direct oxidation of hydrochloric acid. Perchloric acid and chlorine tetroxide result from the decomposition of chloric acid.

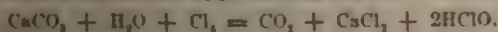
Hypochlorous Oxide, Acid, and Salts.—The oxide is best prepared by the action of chlorine gas upon dry mercuric oxide. This oxide, prepared by precipitation, and dried by exposure to a strong heat, is introduced into a glass tube kept cool, and well-washed dry chlorine gas is slowly passed over it. Mercuric chloride (HgCl_2) and hypochlorous oxide are thereby formed; the latter is collected by displacement. The reaction by which it is produced is represented by the equation,



The mercuric chloride, however, does not remain as such; it combines with another portion of the oxide when the latter is in excess, forming a peculiar brown compound, an oxychloride of mercury, $\text{HgCl}_2 \cdot \text{HgO}$. It is remarkable that the *crystalline* mercuric oxide prepared by calcining the nitrate, or by the direct oxidation of the metal, is scarcely acted upon by chlorine under the circumstances described.

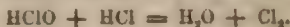
Hypochlorous oxide is a pale-yellow gaseous body, containing, in every two measures, two measures of chlorine and one of oxygen, and is therefore analogous in constitution to water. It explodes, although with no great violence, by slight elevation of temperature. Its odor is peculiar, and quite different from that of chlorine. When the flask or bottle in which the gas is received is exposed to artificial cold by the aid of a mixture of ice and salt, the hypochlorous oxide condenses to a deep-red liquid, slowly soluble in water, and very subject to explosion.

Hypochlorous acid is produced by the solution of hypochlorous oxide in water; also by passing air saturated with hydrochloric acid gas through a solution of potassium permanganate acidulated with hydrochloric acid and heated in a water-bath: the distillate is a solution of hypochlorous acid, formed by oxidation of the hydrochloric acid; thirdly, by decomposing a metallic hypochlorite with sulphuric acid or other oxidant; fourthly, by passing chlorine gas into water holding in suspension a solution containing metallic oxides, hydroxides, carbonates, sulphates, phosphates, etc., the most advantageous for the purpose being mercuric oxide, or calcium carbonate (chalk). CaCO_3 , the products in this case being carbon dioxide, calcium chloride, and hypochlorous acid:



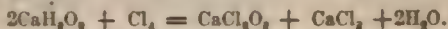
The aqueous solution of hypochlorous acid has a yellowish color, an acid taste, and a characteristic sweetish smell. The strong acid decomposes rapidly even when kept in ice. The dilute acid is more stable, but is de-

composed by long boiling into chloric acid, water, chlorine, and oxygen. Hydrochloric acid decomposes it, with formation of chlorine:



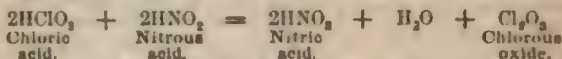
It is a very powerful bleaching and oxidizing agent, converting many of the elements—iodine, selenium, and arsenic, for example—into their highest oxides, and at the same time liberating chlorine.

Metallic hypochlorites may be obtained in the pure state by neutralizing hypochlorous acid with metallic hydroxides, such as those of sodium, calcium, copper, etc.; but they are usually prepared by passing chlorine gas into solutions of alkalies or alkaline carbonates, or over the dry hydroxides of the earth-metals. In this process a metallic chloride is formed at the same time. With dry slaked lime, for example, which is a hydroxide of calcium, CaH_2O_2 , the products are calcium hypochlorite, CaCl_2O_2 , calcium chloride, and water:



The salts thus obtained constitute the bleaching and disinfecting salts of commerce. They will be more fully described under the head of Calcium Salts.

Chlorous Oxide, Acid, and Salts.—The oxide is prepared by heating in a flask filled to the neck, a mixture of four parts of potassium chlorate and 3 parts of arsenious oxide with 12 parts of nitric acid previously diluted with 4 parts of water. During the operation, which must be performed in a water-bath, a greenish-yellow gas is evolved, which is permanent in a freezing mixture of ice and salt, but liquefiable by extreme cold. It dissolves freely in water and in alkaline solutions, forming chlorous acid and metallic chlorites. The reaction by which chlorous oxide is formed is somewhat complicated. The arsenious oxide deprives the nitric acid of part of its oxygen, reducing it to nitrous acid, which is then reoxidized at the expense of the chloric acid, reducing it to chlorous oxide:



Chlorous Acid may be prepared by condensing chlorous oxide in water, or by decomposing a metallic chlorite with dilute sulphuric or phosphoric acid. Its concentrated solution is a greenish-yellow liquid, having strong bleaching and oxidizing properties. It does not decompose carbonates, but acts strongly with caustic alkalies and earths to form chlorites.

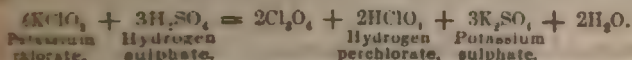
Chlorine Tetroxide, Cl_2O_4 .—When potassium chlorate is made into a paste with concentrated sulphuric acid, and cooled, and this paste is very cautiously heated by warm water in a small glass retort, a deep yellow gas is evolved, which is the body in question; it can be collected only by displacement, since mercury decomposes and water absorbs it.

Chlorine tetroxide has a powerful odor, quite different from that of the preceding compounds, and of chlorine itself. It is exceedingly explosive, being resolved with violence into its elements by a temperature short of the boiling point of water. Its preparation is, therefore, always attended with danger, and should be performed only on a small scale. It is composed by measure of one volume of chlorine and two volumes of oxygen, condensed into two volumes. It may be liquefied by cold. The solution of the gas in water bleaches.

The euchlorine of Davy, prepared by gently heating potassium chlorate

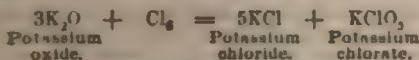
with dilute hydrochloric acid, is probably a mixture of chlorine tetroxide and free chlorine.

The production of chlorine tetroxide from potassium chlorate and sulphuric acid depends upon the spontaneous splitting of the chloric acid into chlorine tetroxide and perchloric acid, which latter remains as a potassium salt.



When a mixture of potassium chlorate and sugar is touched with a drop of oil of vitriol, it is instantly set on fire, the chlorine tetroxide disengaged and decomposed by the combustible substance with such violence as to cause inflammation. If crystals of potassium chlorate be thrown into a pan of water, a few small fragments of phosphorus added, and then oil of vitriol poured down a narrow funnel reaching to the bottom of the glass, the phosphorus will burn beneath the surface of the water, by the assistance of the oxygen of the chlorine tetroxide disengaged. The liquid at the same time becomes yellow, and acquires the odor of that gas.

Chloric Acid, HClO_3 .—This is the most important compound of the acid. When chlorine is passed to saturation into a moderately strong solution of potassium hydroxide or carbonate, and the liquid concentrated by evaporation, it yields, on cooling, flat tabular crystals of a colorless salt, consisting of potassium chlorate. The mother-liquor contains potassium chloride:—



From potassium chlorate, chloric acid may be obtained by boiling the salt with a solution of hydrofluosilicic acid, which forms an almost insoluble potassium salt, decanting the clear liquid, and digesting it with a little silica, which removes the excess of the hydrofluosilicic acid. Filtration through paper must be avoided.

By cautious evaporation, the acid may be so far concentrated as to assume a syrupy consistence; it is then very easily decomposed. It sometimes sets fire to paper, or other dry organic matter, in consequence of the facility with which it is deoxidized by combustible bodies.

The chlorates are easily recognized; they give no precipitate when in solution with silver nitrate; they evolve pure oxygen when heated, passing thereby into chlorides; and they afford, when treated with sulphuric acid, the characteristic explosive yellow gas already described. The dilute solution of the acid has no bleaching power.

Perchloric Acid, HClO_4 .—When powdered potassium chlorate is thrown by small portions at a time into hot nitric acid, a change takes place of the same description as that which happens when sulphuric acid is used, but with this important difference, that the chlorine and oxygen, instead of being evolved in a dangerous state of combination, are emitted in a state of mixture. The result of the action is a mixture of potassium nitrate and perchlorate, which may be readily separated by their difference of solubility.

Perchloric acid is obtained by distilling potassium perchlorate with sulphuric acid. Pure perchloric acid is a colorless liquid, of 1.782 sp. gr. at 15.5°C . (60°F .), not solidifying at -35°C . (-31°F .); it soon becomes colored, even if kept in the dark, and after a few weeks decomposes with

explosion. The vapor of perchloric acid is transparent and colorless: in contact with moist air, it produces dense white fumes. The acid, when cautiously mixed with a small quantity of water, solidifies to a crystalline mass, which is a compound of perchloric acid with one molecule of water, $\text{HClO}_4 + \text{H}_2\text{O}$. When brought in contact with carbon, ether, or other organic substances, perchloric acid explodes with nearly as much violence as chloride of nitrogen.

Compound of Chlorine and Nitrogen, NCl_3 .—When sal-ammoniac or ammonia nitrate is dissolved in water, and a jar of chlorine inverted in the solution, the gas is absorbed, and a deep yellow oily liquid is observed to collect upon the surface of the solution, ultimately sinking in globules to the bottom. This is nitrogen chloride, one of the most dangerously explosive substances known. The following is the safest method of conducting the experiment:—

A somewhat dilute and tepid solution of pure sal-ammoniac in distilled water is poured into a clean basin, and a bottle of chlorine, the neck of which is quite free from grease, inverted in it. A shallow and heavy leaden cup is placed beneath the mouth of the bottle to collect the product. When enough has been obtained, the leaden vessel may be withdrawn with its dangerous contents, the chloride remaining covered with a stratum of water. The operator should protect his face with a strong wire-gauze mask when experimenting upon this substance.

The change may be explained by the equation—



Nitrogen chloride is very volatile, and its vapor is exceedingly irritating to the eyes. It has a specific gravity of 1.653. It may be distilled at 71°C . (160°F .), although the experiment is attended with great danger. Between 93°C . (200°F .) and 105°C . (221°F .) it explodes with the most fearful violence. Contact with almost any combustible matter, as oil or fat of any kind, determines the explosion at common temperatures; a vessel of porcelain, glass, or even of cast-iron, is broken to pieces, and the leaden cup receives a deep indentation. This body has usually been supposed to contain nitrogen and chlorine in the proportion of 14 parts of the former to 106.5 parts of the latter, but recent experiments upon the corresponding iodine compound (p. 188) induce a belief that it contains hydrogen.*

Chlorine and Carbon.—Several compounds of chlorine and carbon are known, namely, C_2Cl_2 , C_2Cl_4 , C_2Cl_6 , and CCl_4 . They are obtained indirectly by the action of chlorine upon certain organic compounds, and will be described under Organic Chemistry.

The *Oxychloride of Carbon*, COCl_2 , called also *Carbonyl Chloride* and *Phosgene*, has been already mentioned (p. 164).

BROMINE.

Atomic weight, 80. Symbol, Br.

Bromine† was discovered by Balard in 1826. It is found in sea-water, and is a frequent constituent of saline springs, chiefly as magnesium brie-

* Instead of NCl_3 , it may in reality be NHCl_2 or NH_2Cl .

† From *ερμαρ*, a noisome smell.

side: a celebrated spring of the kind exists near Kreuznach, in Prussia. Arsenic may be obtained pure by the following process, which depends upon the fact that ether, agitated with an aqueous solution of bromine, removes the greater part of that substance.

The mother-liquor, from which the less soluble salts have separated by crystallization, is exposed to a stream of chlorine, and then shaken up with ether; the chlorine decomposes the magnesium bromide, and the ether dissolves the bromine thus set free. On standing, the ethereal solution, having a fine red color, separates, and may be removed by a funnel and pipette. Caustic potash is then added in excess, and heat applied; bromide and bromate of potassium are formed. The solution is evaporated to dryness, and the saline matter, after ignition to redness to decompose bromate, is heated in a small retort with manganese dioxide and sulphuric acid diluted with a little water, the neck of the retort being plunged in cold water. The bromine volatilizes in the form of a deep red vapor, and condenses into drops beneath the liquid.

Bromine is at common temperatures a thin red liquid of an exceedingly strong color, and very volatile; it freezes at about -24.5°C . (-12.1°F .) and boils at 63°C . (143°F .). The density of the liquid is 2.976, and that of the vapor 5.54 compared with air, and 80 compared with hydrogen. The odor of bromine is very suffocating and offensive, much resembling that of iodine, but more disagreeable. It is slightly soluble in water, more so in alcohol, and most abundantly in ether. The aqueous solution is called.

Hydrogen Bromide, or Hydrobromic Acid, HBr .—This substance has the closest resemblance to hydriodic acid: it has the same constitution by volume, very nearly the same properties, and may be prepared by means exactly similar, substituting the one body for the other (see page 181). The solution of hydrobromic acid has also the power of dissolving a large quantity of bromine, thereby acquiring a red tint. Hydrobromic acid contains by weight 80 parts bromine and 1 part hydrogen.

Bromic Acid, HBrO_3 .—Caustic alkalis in presence of bromine undergo the same change as with chlorine, a metallic bromide and bromate being produced; these may be separated by the inferior solubility of the latter. Bromic acid, obtained from barium bromate, closely resembles chloric acid; it is easily decomposed. The bromates, when heated, lose oxygen and become bromides.

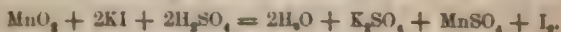
A hypobromous acid corresponding with hypochlorous acid is likewise known.

IODINE.

Atomic weight, 127. Symbol, I .

This element was first noticed in 1812 by M. Courtois, of Paris. Minute traces are found in combination with sodium or potassium in sea-water, and occasionally a much larger proportion in that of certain mineral springs. It seems to be in some way beneficial to many marine plants, as these latter have the power of abstracting it from the surrounding water, and accumulating it in their tissues. It is from this source that all the iodine of commerce is derived. It has lately been found in minute quantity in some aluminous slates of Sweden, and in several varieties of coal and turf.

Kelp, or the half-vitrified ashes of sea-weeds, prepared by the inhabitants of the Western Islands and the northern shores of Scotland and Ireland, is treated with water, and the solution filtered. The liquid is then concentrated by evaporation until it is reduced to a very small volume, the sodium chloride, sodium carbonate, potassium chloride, and other salts being removed as they successively crystallize. The dark-brown mother-liquor left contains very nearly the whole of the iodine, as iodide of sodium, magnesium, etc. : this is mixed with sulphuric acid and manganese dioxide, and gently heated in a leaden retort, when the iodine distils over and condenses in the receiver. The theory of the operation is exactly analogous to that of the preparation of chlorine (p. 176); in practice, however, it requires careful management, otherwise the impurities present in the solution interfere with the general result:



The manganese is not absolutely necessary: potassium or sodium iodide, heated with an excess of sulphuric acid, evolves iodine. This effect is due to a secondary action between the hydriodic acid first produced and the excess of the sulphuric acid, in which both suffer decomposition, yielding iodine, water, and sulphurous acid.

Iodine crystallizes in plates or scales of a bluish-black color and imperfect metallic lustre, resembling that of plumbago: the crystals are sometimes very large and brilliant. Its density is 4.948. It melts at 107°C . (225°F .), and boils at 175°C . (347°F .), the vapor having an exceedingly beautiful violet color.* It is slowly volatile, however, at common temperatures, and exhales an odor much resembling that of chlorine. The density of the vapor is 8.716 compared with air, 127 compared with hydrogen. Iodine requires for solution about 7000 parts of water, which nevertheless acquires a brown color; in alcohol it is much more freely soluble. Solutions of hydriodic acid and the iodides of the alkali-metals also dissolve a large quantity: these solutions are not decomposed by water, which is the case with the alcoholic tincture.

Iodine stains the skin, but not permanently; it has a very energetic action upon the animal system, and is much used in medicine.

One of the most characteristic properties of iodine is the production of a splendid blue color by contact with starch. The iodine for this purpose must be free or uncombined. It is easy, however, to make the test available for the purpose of recognizing the presence of the element in question when a soluble iodide is suspected; it is only necessary to add a very small quantity of chlorine-water, when the iodine, being displaced from combination, becomes capable of acting upon the starch.

Hydrogen Iodide, or Hydriodic Acid, III.—The simplest process for preparing hydriodic acid gas is to introduce into a glass tube, sealed at once extremity, a little iodine, then a small quantity of roughly-powdered glass moistened with water, upon this a few fragments of phos-

Fig. 124.



* Whence the name, from *ios*, violet-colored.

phorus, and lastly, more glass, this order of iodine, glass, phosphorus, glass, being repeated until the tube is half or two-thirds filled. A cork and narrow bent tube are then fitted, and gentle heat applied. The gas is best collected by displacement of air. The process depends on the formation of an iodide of phosphorus and its subsequent decomposition by water, whereby hydrogen phosphite, or phosphorous acid, H_2PO_3 , and hydrogen iodide are produced: $\text{P}_2 + \text{I}_2 + 6\text{H}_2\text{O} = 6\text{HI} + 2\text{H}_2\text{PO}_3$. The glass merely serves to moderate the violence of the action of the iodine upon the phosphorus.

Hydriodic acid gas greatly resembles the corresponding chlorine compound; it is colorless, and highly acid; it fumes in the air, and is very soluble in water. Its density is about 4.4 compared with air, 64 compared with hydrogen. By weight, it is composed of 127 parts iodine and 1 part hydrogen; and by measure of equal volumes of iodine vapor and hydrogen united without condensation.

Solution of hydriodic acid may be prepared by a process much less troublesome than the above. Iodine in fine powder is suspended in water, and a stream of washed hydrogen sulphide passed through the mixture; sulphur is deposited, and the iodine converted into hydriodic acid. When the liquid has become colorless, it is heated, to expel the excess of hydrogen sulphide, and filtered. The solution cannot be kept long, especially if it be concentrated; the oxygen of the air gradually decomposes the hydriodic acid, and iodine is set free, which, dissolving in the remainder, communicates to it a brown color.

Compounds of Iodine and Oxygen.

The most important of these are the iodic and periodic oxides.

| | | Composition by weight. | | | |
|--|---|------------------------|-----|---------|-----|
| | | Iodine. | | Oxygen. | |
| Iodic oxide, I_2O_5 | . | 2 | 127 | + | 80 |
| Periodic oxide, I_2O_7 | . | 2 | 127 | + | 112 |

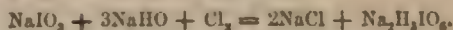
Both these are acid oxides, uniting with water and metallic oxides, and forming salts called iodates and periodates.

Hydrogen Iodate, or Iodic Acid, $\text{H}_2\text{O.I}_2\text{O}_5$, or HIO_3 , may be prepared by the direct oxidation of iodine with nitric acid of specific gravity 1.5. Five parts of dry iodine with 200 parts of nitric acid are kept at a boiling temperature for several hours, or until the iodine has disappeared. The solution is then cautiously distilled to dryness, and the residue dissolved in water and made to crystallize.

Iodic acid is a very soluble substance, crystallizing in colorless six-sided tables. At 107° it is resolved into water and iodic oxide, which forms tabular rhombic crystals, and when heated to the temperature of boiling olive oil, is completely resolved into iodine and oxygen. The solution of iodic acid is readily deoxidized by sulphurous acid. The iodates much resemble the chlorates; that of potassium is decomposed by heat into potassium iodide and oxygen gas.

Hydrogen Periodate, or Periodic Acid, $\text{H}_2\text{O.I}_2\text{O}_7$, or HIO_4 .—When solution of sodium iodate is mixed with caustic soda, and a current of chlorine passed through the liquid, two salts are formed—namely, sodium chloride and a sparingly soluble compound of sodium periodate with

sodium hydroxide and water, $\text{NaIO}_4 \cdot \text{NaHO} \cdot \text{H}_2\text{O}$, or $\text{Na}_2\text{H}_2\text{IO}_6$, the reaction taking place as represented by the equation—



This sodium salt is separated, converted into a silver salt, and dissolved in nitric acid: the solution yields, on evaporation, crystals of yellow silver periodate, from which the acid may be separated by the action of water, which resolves the salt into free acid and an insoluble basic periodate.

Periodic acid crystallizes from its aqueous solution in deliquescent oblique rhombic prisms, which melt at 130°C . (266°F .), and are resolved at 170°C . (338°F .) into water and a white mass of periodic oxide, which at 180° or 190°C . (356 – 374°F .) gives off oxygen with great rapidity, and iodic oxide.

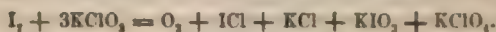
The solution of periodic acid is reduced by many organic substances, and instantly by hydrochloric acid, sulphurous acid, and hydrogen sulphide. With hydrochloric acid it forms water, iodine chloride, and free chlorine. The metallic periodates are resolved by heat into oxygen and metallic iodide.

Compounds of Iodine and Nitrogen.—When finely powdered iodine is put into caustic ammonia, it is in part dissolved, giving a deep-brown solution, and the residue is converted into a black powder, called nitrogen iodide, NI_3 . The brown liquid consists of hydriodic acid holding iodine in solution, and is easily separated from the solid product by a filter. The latter, while still wet, is distributed in small quantities upon separate pieces of bibulous paper, and left to dry in the air.

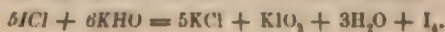
Nitrogen iodide is a black insoluble powder, which, when dry, explodes with the slightest touch—even that of a feather—and sometimes without any obvious cause. The explosion is, however, not nearly so violent as that of nitrogen chloride, and is attended with the production of violet fumes of iodine. According to Dr. Gladstone, this substance contains hydrogen, and may be viewed as NHI_3 , that is, as ammonia in which two-thirds of the hydrogen are replaced by iodine. According to the researches of Bunsen, it must be viewed as a combination of nitrogen tri-iodide with ammonia, $\text{NI}_3 \cdot \text{NH}_3$. It appears, however, that the substance called nitrogen iodide varies in composition. Gladstone, by changing the mode of preparation, obtained several compounds of nitrogen tri-iodide with ammonia.

Compounds of Iodine and Chlorine.—Iodine unites directly with chlorine, forming a monochloride and a trichloride. There is also a tetrachloride produced by spontaneous decomposition of the monochloride.

The monochloride, ICl , is obtained by passing dry chlorine over iodine till the whole is liquefied, but no longer; also by distilling iodine with potassium chlorate, oxygen being then evolved, the monochloride distilling over, and a mixture of chloride, iodate, and perchlorate of potassium remaining behind.



Iodine monochloride is a reddish-brown oily liquid, having a suffocating odor and astringent taste; soluble in alcohol and ether; decomposed by water, with formation of hydrochloric and iodic acids, and separation of iodine. It sometimes solidifies in yellow needles. Sulphurous acid and hydrogen sulphide decompose it, with separation of iodine; with aqueous solutions of alkalis, it yields a chloride and an iodate, together with free iodine; thus, with potash—

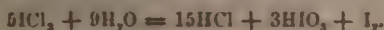


The *trichloride*, ICl_3 , is produced by treating iodine at a gentle heat with chlorine in excess. It crystallizes in orange-yellow needles; melts at 200°C . ($388\text{--}377^\circ \text{F}$.), giving off chlorine, which it reabsorbs on cooling; acts on most other substances like the monochloride.

In contact with a small quantity of water it is partly resolved into an insoluble yellowish body (probably a mixture of the trichloride with iodic oxide), and a solution containing hydrochloric acid and the monochloride—



A large quantity of water dissolves it, probably without decomposition, or perhaps as a mixture of hydrochloric and iodic acids containing free iodine—



The *tetrachloride*, ICl_4 , produced by spontaneous decomposition of the monochloride, $4\text{ICl} = \text{ICl}_4 + \text{I}_2$, crystallizes in red octohedrons.

FLUORINE.

Atomic weight, 19. Symbol, F.

This element has never been isolated—at least, in a state fit for examination; its properties are consequently in great measure unknown: but from the observations made, it is presumed to be gaseous, and to possess color, like chlorine. The compounds containing fluorine can be easily decomposed, and the element transferred from one body to another; but its intense chemical energies towards the metals and towards silicium, a component of glass, have hitherto baffled all attempts to obtain it pure in the separate state. As calcium fluoride, it exists in considerable quantities as fluor-spar, a mineral which crystallizes in fine cubes of various colors, and in small quantities in many animal substances, such as bones. Several chemists have endeavored to obtain it by decomposing silver fluoride by means of chlorine in vessels of fluor-spar, but even these experiments have not led to a decisive result.

Hydrogen Fluoride, or Hydrofluoric Acid, HF.—When powdered calcium fluoride is heated with concentrated sulphuric acid in a retort of platinum or lead connected with a carefully cooled receiver of the same metal, a very volatile colorless liquid is obtained, which emits copious white and highly suffocating fumes in the air. This is the anhydrous acid, not however quite pure. It may be obtained in a state of perfect purity by distilling hydrogen-potassium fluoride, HF.KF , to redness in a platinum vessel. As thus prepared, it is at ordinary temperatures a colorless, transparent, mobile liquid, having a specific gravity of 0.9879 at 12.8°C . (55°F .), extremely volatile, boiling at 19.4°C . (66.9°F .), fuming densely at ordinary temperatures, and absorbing water greedily from the air.* It contains 19 parts by weight of fluorine to 1 part of hydrogen.

When hydrofluoric acid is put into water, it unites with the latter with great violence; the dilute solution attacks glass with great facility. The concentrated acid, dropped upon the skin, occasions deep and malignant

* Gore, *Journal of the Chemical Society* [2], ii. 368.

ulcers, so that great care is requisite in its management. Hydrofluoric acid contains 19 parts fluorine and 1 part hydrogen.

In a diluted state, this acid is occasionally used in the analysis of siliceous minerals, when alkali is to be estimated. It is employed also for etching on glass, for which purpose the acid may be prepared in vessels of lead, that metal being but slowly attacked under these circumstances. The vapor of the acid is also very advantageously applied to the same purpose in the following manner: The glass to be engraved is coated with etching-ground or wax, and the design traced in the usual way with a pointed instrument. A shallow basin, made by beating up a piece of sheet-lead, is then prepared, a little powdered fluor-spar placed in it, and enough sulphuric acid added to form with the latter a thin paste. The glass is placed upon the basin, with the waxed side downwards, and gentle heat applied beneath, which speedily disengages the vapor of hydrofluoric acid. In a very few minutes the operation is complete; the glass is then removed, and cleaned by a little warm oil of turpentine. When the experiment is successful, the lines are very clean and smooth.

No combination of fluorine and oxygen has yet been discovered.

SULPHUR.

Atomic weight, 32. Symbol, S.

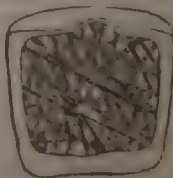
This is an elementary body of great importance and interest. It is often found in the free state in connection with deposits of gypsum and rock-salt, and in the fissures of volcanic craters. Sicily furnishes a large proportion of the sulphur employed in Europe. Sulphur also occurs abundantly in combination with iron and other metals, and as sulphuric acid, united to lime and magnesia.

Pure sulphur is a pale-yellow brittle solid, of well-known appearance. It melts when heated, and distils over unaltered, if air be excluded. The crystals of sulphur exhibit two distinct and incompatible forms—namely, first, an octohedron with rhombic base (fig. 125), which is the figure of native sulphur, and that assumed when sulphur separates from solution at common temperatures, as when a solution of sulphur in carbon bisulphide is exposed to slow evaporation in the air; and, secondly, a lengthened prism having no relation to the preceding; this happens when a mass

Fig. 125.



Fig. 126.



of sulphur is melted, and, after partial cooling, the crust on the surface is broken, and the fluid portion poured out. Fig. 126 shows the result of such an experiment.

The specific gravity of sulphur varies according to the form in which it is crystallized. The octohedral variety has the specific gravity 2.045, the prismatic variety the specific gravity 1.982.

Sulphur melts at 111° C. (232° F.),—at 114.5° C. (238.1° F.), according to Brönne, at this temperature it is of the color of amber, and thin and fluid as water; when further heated, it begins to thicken, and to acquire a deeper color; and between 221° C. (430° F.) and 249° C. (480° F.) it is so tenacious that the vessel in which it is contained may be inverted for a moment without the loss of its contents. If in this state it be poured into water, it retains for many hours a remarkably soft and flexible condition, which may be looked upon as the amorphous state of sulphur. After a while it again becomes brittle and crystalline. From the temperature last mentioned to the boiling-point—about 400° C. (702° F.)—sulphur again becomes thin and liquid. In the preparation of commercial flowers of sulphur, the vapor is conducted into a large cold chamber, where it condenses in minute crystals. The specific gravity of sulphur vapor is 2.22 referred to that of air as unity, or 32 compared with that of hydrogen (Dewille).

Sulphur is insoluble in water and alcohol; oil of turpentine and the fat oils dissolve it, but the best substance for the purpose is carbon bisulphide. In its chemical relations, sulphur bears great resemblance to oxygen: to very many oxides there are corresponding sulphides, and the sulphides often unite among themselves, forming crystallizable compounds analogous to oxysalts.

Sulphur is remarkable for the great number of modifications which it is capable of assuming. Of these, however, there are two principal well-characterized varieties, one soluble, and the other insoluble in carbon bisulphide, and many minor modifications. The soluble variety is distinguished by Berthelot by the name of *electro-negative sulphur*, because it is the form which appears at the positive pole of the voltaic battery during the decomposition of an aqueous solution of hydrogen sulphide, and is separated from the combinations of sulphur with the electro-positive metals. The insoluble variety is distinguished as *electro-positive sulphur*, because it is the form which appears at the negative pole during the electro-decomposition of sulphurous acid, and separates from compounds of sulphur with the electro-negative elements, chlorine, bromine, oxygen, etc.

The principal modifications of soluble sulphur are the octohedral and prismatic varieties already mentioned, and an amorphous variety which is precipitated as a greenish-white emulsion, known as milk of sulphur, on adding an acid to a dilute solution of an alkaline polysulphide, such, for example, as is obtained by boiling sulphur with milk of lime. This amorphous sulphur changes by keeping into a mass of minute octohedral crystals. Sublimed sulphur appears also to be allied to this modification, but it always contains a small portion of one of the insoluble modifications.

The chief modifications of insoluble sulphur are: 1. The amorphous insoluble variety, obtained as a soft magma by decomposing chlorine bisulphide with water, or by adding dilute hydrochloric acid to the solution of a thiosulphate (p. 198). 2. The plastic sulphur already mentioned as obtained by pouring viscid melted sulphur into water. A very similar variety is produced by boiling metallic sulphides with nitric or nitrosulphuric acid.

When solutions of hydrogen sulphide and ferric chloride are mixed together, a blue precipitate is sometimes formed, which is said to be a peculiar modification of sulphur.

Compounds of Sulphur and Oxygen.

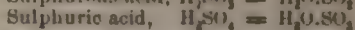
There are two oxides of sulphur, whose names and composition are as follows :—

| | Composition by weight. | | |
|--|------------------------|---------|----|
| | Sulphur. | Oxygen. | |
| Sulphur dioxide or Sulphurous oxide, SO_2 . | 32 | + | 32 |
| Sulphur trioxide or Sulphuric oxide, SO_3 . | 32 | + | 48 |

Both these oxides unite with water and metallic oxides, or the elements thereof, producing salts; those derived from sulphurous oxide are called sulphites, and those derived from sulphuric acid, sulphates. The composition of the hydrogen salts or acids is as follows :—

| | Hydrogen. | Sulphur. | Oxygen. | Water. | Sulphurous oxide. |
|---|-----------|----------|---------|--------|-------------------|
| Hydrogen Sulphite, or }
Sulphurous acid, | 2 | + | 32 | + | 48 = 18 + 64 |
| | | | | Water. | Sulphuric oxide. |
| Hydrogen Sulphate, }
or Sulphuric acid, | 2 | + | 32 | + | 64 = 18 + 80 |

The formulae of these acids are—



The replacement of half or the whole of the hydrogen by metals gives rise to metallic sulphites and sulphates.

By the combination of sulphuric oxide with sulphuric acid in the proportion of SO_3 to H_2SO_4 (or 80 parts by weight of the oxide to 98 of the acid) an acid is formed called disulphuric or pyrosulphuric acid, having the composition $\text{H}_2\text{S}_2\text{O}_7$, or

| Hydrogen. | Sulphur. | Oxygen. |
|-----------|----------|----------|
| 2 | + | 64 + 112 |

There are also several acids of sulphur, with their corresponding metallic salts, to which there are no corresponding anhydrous oxides, viz. :—

1. *Hyposulphurous Acid*, H_2SO_2 , having the composition of sulphurous acid minus one atom of oxygen. Its composition by weight is—

| Hydrogen. | Sulphur. | Oxygen. |
|-----------|----------|---------|
| 2 | + | 32 + 32 |

2. *Thiosulphuric Acid*, $\text{H}_2\text{S}_2\text{O}_3$, having the composition of sulphuric acid in which one-fourth of the oxygen is replaced by sulphur. Its composition by weight is—

| Hydrogen. | Sulphur. | Oxygen. |
|-----------|----------|---------|
| 2 | + | 64 + 48 |

Closely allied to this acid is—

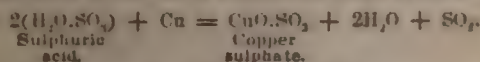
3. *Seleniosulphuric Acid*, H_2SSeO_6 , having the composition of sulphuric acid in which one-fourth of the oxygen is replaced by selenium. Its composition by weight is—

| Hydrogen. | Sulphur. | Selenium. | Oxygen. |
|-----------|----------|-----------|---------|
| 2 | + | 32 + 79.4 | + 48 |

4. A series of acids called *Polythionic Acids*,* in which the same quantities of oxygen and hydrogen are united with quantities of sulphur in the proportion of the numbers 2, 3, 4, 5, viz. :—

| | | Hydrogen. | Sulphur. | Oxygen. | | | |
|---|------------------------------------|-------------------------------------|----------|---------|-----|----|----|
| Dithionic, or Hypo-
sulphuric acid . . . | } $\text{H}_2\text{S}_2\text{O}_3$ | 2 | + | 64 | + | 96 | |
| Trithionic acid . . . | | $\text{H}_2\text{S}_3\text{O}_6$ | 2 | + | 96 | + | 96 |
| Tetrathionic acid . . . | | $\text{H}_2\text{S}_4\text{O}_8$ | 2 | + | 128 | + | 96 |
| Pentathionic acid . . . | | $\text{H}_2\text{S}_5\text{O}_{10}$ | 2 | + | 150 | + | 96 |

Sulphur Dioxide, or Sulphurous Oxide, SO_2 .—This is the only product of the combustion of sulphur in dry air or oxygen gas. It is most conveniently prepared by heating sulphuric acid with metallic mercury or copper clippings. A portion of the acid is decomposed, one-third of the oxygen of the sulphuric oxide being transferred to the metal, while the sulphuric oxide is reduced to sulphurous oxide which escapes as gas :



Another very simple method of preparing sulphurous oxide consists in heating concentrated sulphuric acid with sulphur ; a very regular evolution of sulphurous oxide is thus obtained.

Sulphurous oxide is a colorless gas, having the peculiar suffocating odor of burning brimstone ; it instantly extinguishes flame, and is quite irreparable. Its density is 2.21 ; a litre weighs 2.8605 grams ; 100 cubic inches weigh 68.69 grains. At -17.8°C . (0°F .), under the ordinary pressure of the atmosphere, this gas condenses to a colorless, limpid liquid, very expansible by heat. Cold water dissolves more than thirty times its volume of sulphurous oxide. The solution, which contains hydrogen sulphate or sulphurous acid, may be kept unchanged so long as air is excluded, but access of oxygen gradually converts the sulphurous into sulphuric acid, although dry sulphurous oxide and oxygen gases may remain in contact for any length of time without change. When sulphurous oxide and aqueous vapor are passed into a vessel cooled to below -8.3° or -5°C . (17° or 21°F .), a crystalline body forms, which contains about 34.2 sulphurous oxide to 75.8 of water.

One volume of sulphurous oxide gas contains one volume of oxygen and half a volume of sulphur vapor, condensed into one volume.

Sulphurous oxide, like other gases which are freely soluble in water, must be collected by displacement, or by the use of the mercurial pneumatic trough. The manipulation with the latter is exactly the same in principle as with the ordinary water trough, but rather more troublesome, from the great density of the mercury, and its opacity. The whole apparatus is on a much smaller scale. The trough is best constructed of hard, sound wood, and so contrived as to economize as much as possible the expensive liquid it is to contain.

Sulphurous acid has bleaching properties ; it is used in the arts for bleaching woollen goods and straw-plait. A piece of blue litmus-paper plunged into the moist gas is first reddened and then slowly bleached.

The sulphates of the alkalis are soluble and crystallizable ; they are easily formed by direct combination. The sulphites of barium, strontium, and calcium are insoluble in water, but soluble in hydrochloric acid. The stronger acids decompose them ; nitric acid converts them into sul-

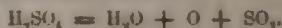
* From *wele*, many, and *thion*, sulphur.

phates. The soluble sulphites act as powerful reducing agents, and are much used in that capacity in chemical analysis.

Sulphurous oxide unites, under peculiar circumstances, with chlorine, and also with iodine, forming compounds which have been called chloro- and iodo-sulphuric acids. They are decomposed by water. It also combines with dry ammoniacal gas; and with nitric oxide in presence of an alkali.

Sulphur Trioxide, or Sulphuric Oxide, SO_3 (also called *Anhydrous Sulphuric acid*, or *Sulphuric anhydride*).—This compound may be formed directly by passing a dry mixture of sulphurous oxide and oxygen gases over heated spongy platinum; or it may be obtained by distilling the most concentrated sulphuric acid with phosphoric oxide, which then abstracts the water and sets the sulphuric oxide free. It is usually prepared, however, from the fuming oil of vitriol of Nordhausen, which may be regarded as a solution of sulphuric oxide in sulphuric acid. On gently heating this liquid in a retort connected with a receiver cooled by a freezing mixture, the sulphuric oxide distils over in great abundance, and condenses into beautiful white silky crystals, resembling those of asbestos.

Sulphuric oxide is also produced in considerable quantity by the following process. Vapor of ordinary strong sulphuric acid is passed through a white-hot platinum tube, whereby it is almost completely resolved into water, oxygen, and sulphurous oxide:—



These mixed gases, after passing through a leaden worm to condense the greater portion of the water, are dehydrated by passing them through a leaden tower filled with coke, over which a stream of concentrated sulphuric acid is allowed to trickle; and, finally, the dry mixture of oxygen and sulphurous oxide is passed through platinum tubes heated to low redness and containing fragments of platinized purice, whereupon they recombine to form sulphuric oxide, which is condensed in a series of Woulfe's bottles. This process bids fair to succeed as a manufacturing operation.*

Sulphuric oxide, when thrown into water, hisses like a red-hot iron, from the violence with which combination occurs: the product is sulphuric acid. When exposed to the air, even for a few moments, it liquefies by absorption of moisture. It unites with ammoniacal gas, forming a salt called ammonium sulphamate, the nature of which will be explained further on.

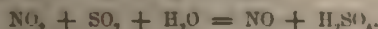
Sulphuric oxide is susceptible of two modifications (*a* and *β*), differing in their properties, though identical in composition. Bodies thus related are said to be isomeric (from *isos*, equal, and *meros*, part). There are but few examples of this relation amongst inorganic compounds, but it is of frequent occurrence in organic chemistry. The *a*-modification, formed by cooling the liquid oxide, solidifies at $+16^\circ$ in long colorless prisms, which melt at the same temperature; it boils at 46° ; and its vapor at 20° has a tension represented by 200 millimetres of mercury. *β*-Sulphuric oxide is produced from the *a*-modification at temperatures below 25° ; above 27° the transformation does not go on. It forms extremely fine white needles, at temperatures above 50° it gradually liquefies and passes into the first modification. Liquid sulphuric oxide undergoes very great expansion by heat, its mean co-efficient of expansion between 25° and 45° being 0.0027 for 1°C ., that is to say, more than two-thirds as great as that of gases. The two modifications differ greatly in their relations to solvents. Liquid sulphuric oxide mixes in all proportions with hydrogen sulphate, H_2SO_4 ;

* Nessel and Squire, Chemical News, 1876, vii.

the δ -oxide dissolves in sulphuric acid with extreme slowness, and gradually separates from a mixture of 10 parts SO_2 and 1-2 parts H_2SO_4 . With a larger proportion of the acid, no solid oxide separates, even on cooling to a low temperature, if the proportion of acid, H_2SO_4 , amounts to 5 parts for 10 parts of oxide, the liquid may deposit crystals of pyrosulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$ or $\text{H}_2\text{SO}_4\cdot\text{SO}_3$.

Sulphuric Acid, H_2SO_4 .—The preparation of this important acid depends upon the fact that, when sulphurous oxide, nitrogen tetroxide, and water are present together in certain proportions, the sulphurous oxide becomes oxidized at the expense of the nitrogen tetroxide, which, by the loss of one-half of its oxygen, sinks to the condition of nitrogen dioxide. The operation is thus conducted :—

A large and very long chamber is built of sheet-lead supported by timber framing ; on the outside, at one extremity, a small furnace or oven is constructed, having a wide tube leading into the chamber. In this, sulphur is kept burning, the flame of which heats a crucible containing a mixture of nitre and oil of vitriol. A shallow stratum of water occupies the floor of the chamber, and a jet of steam is also introduced. Lastly, an exit is provided at the remote end of the chamber for the spent and useless gases. The effect of these arrangements is to cause a constant supply of sulphurous oxide, atmospheric air, nitric acid vapor, and water at the state of steam, to be thrown into the chamber, there to mix and react upon each other. The nitric acid immediately gives up a part of its oxygen to the sulphurous oxide, and is itself reduced to nitrogen tetroxide, N_2O_4 or NO_2 ; it does not remain in this state, however, but suffers further oxidation until it becomes reduced to nitrogen dioxide, N_2O_2 or NO . That substance, in contact with free oxygen, absorbs a portion of the latter, and once more becomes tetroxide, which is again destined to undergo de-oxidation by a fresh quantity of sulphurous oxide. A very small portion of nitrogen tetroxide, mixed with atmospheric air and sulphurous oxide, may thus in time convert an indefinite amount of the latter into sulphuric acid, by acting as a kind of carrier between the oxygen of the air and the sulphurous oxide. The presence of water is essential to this reaction, which may be represented by the equation,



Such is the simplest view that can be taken of the production of sulphuric acid in the leaden chamber ; but it is too much to affirm that it is strictly true ; the reaction may be more complex. When a little water is put at the bottom of a large glass globe, so as to maintain a certain degree of humidity in the air within, and sulphurous oxide and nitrogen tetroxide are introduced by separate tubes, symptoms of chemical action become immediately evident, and after a little time a white crystalline matter is observed to condense on the sides of the vessel. This substance appears to be a compound of sulphuric acid, nitrous acid, and a little water.*

* Oaultier de Claubry assigned to this substance the composition expressed by the formula $2(\text{N}_2\text{O})\cdot 2\text{H}_2\text{O}\cdot 5\text{SO}_3$, and this view has generally been received by recent chemical writers. De la Provostaye has since shown that a compound possessing all the essential properties of the body in question may be formed by bringing together, in a sealed glass tube, liquid sulphurous oxide and liquid nitrogen tetroxide, both free from water. The white crystalline solid soon begins to form, and at the expiration of twenty-six hours, the reaction appears complete. The new product is accompanied by an exceedingly volatile greenish liquid having the characters of nitrous acid. The white substance, on analysis, was found to contain the elements of two molecules of sulphuric oxide, and one of nitrous oxide, or $\text{N}_2\text{O}\cdot 2\text{SO}_2$. De la Provostaye explains the anomalies in the different analyses of the leaden chamber product, by showing that the pure substance forms variable combinations with different proportions of sulphuric acid. (Ann. Chim. Phys. [sixt] 352. See also Weber, Jahresbericht für Chemie, 1863, p. 748 ; 1864, p. 63, Bull. Soc. Chim. de Paris, 1867, 1, 16).

When thrown into water, it is resolved into sulphuric acid, nitrogen dioxide, and nitric acid. This curious body is certainly very often produced in large quantity in the leaden chambers; but that its production is indispensable to the success of the process, and constant when the operation goes on well and the nitrogen tetroxide is not in excess, may perhaps admit of doubt.

The water at the bottom of the chamber thus becomes loaded with sulphuric acid; when a certain degree of strength has been reached, the acid is drawn off and concentrated by evaporation, first in leaden pans, and afterwards in stills of platinum, until it attains a density (when cold) of 1.84, or thereabouts; it is then transferred to carboys, or large glass bottles fitted in baskets, for sale. In Great Britain this manufacture is one of great national importance, and is carried on to a vast extent.

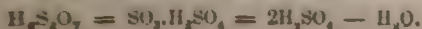
Sulphuric acid is now more frequently made by burning iron pyrites, or poor copper ore, or zinc-blende, instead of Sicilian sulphur: as thus prepared it very frequently contains arsenic, from which it may be freed, however, by heating it with a small quantity of sodium chloride, or by passing through the heated acid a current of hydrochloric acid gas, whereby the arsenic is volatilized as trichloride.

The most concentrated sulphuric acid, or *oil of vitriol*, as it is often called, is a definite combination of 40 parts sulphuric oxide and 9 parts of water, and is represented by the formula $H_2O.SO_3$, or H_2SO_4 . It is a colorless oily liquid, having a specific gravity of about 1.85, of intensely acid taste and reaction. Organic matter is rapidly charred and destroyed by it. At the temperature of $-26^\circ C.$ ($-15^\circ F.$) it freezes; at $327^\circ C.$ ($620^\circ F.$) it boils, and may be distilled without decomposition. Oil of vitriol has a most energetic attraction for water: it withdraws aqueous vapor from the air, and when it is diluted with water, great heat is evolved, so that the mixture always requires to be made with caution. Oil of vitriol is not the only hydrate of sulphuric oxide; three others are known to exist. When the fuming oil of vitriol of Nordhausen is exposed to a low temperature, a white crystalline substance separates, which is a hydrate containing half as much water as the common liquid acid. Further, a mixture of 28 parts of strong liquid acid and 18 parts of water, $2H_2O.SO_3$ or $H_2SO_4.H_2O$, congeals or crystallizes at a temperature above $0^\circ C.$, and remains solid even at $7.2^\circ C.$ ($45^\circ F.$). Lastly, when a very dilute acid is concentrated by evaporation in a vacuum over a surface of oil of vitriol, the evaporation stops when the sulphuric oxide and water bear to each other the proportion of 80 to 54, answering to the formula, $3H_2O.SO_3$ or $H_2SO_4.2H_2O$.

When the vapor of sulphuric acid is passed over red-hot platinum, it is decomposed into oxygen and sulphurous acid. St. Claire Deville and Debray have recommended this process for the preparation of oxygen on the large scale, the sulphurous acid being easily separated by its solubility in water or alkaline solutions.

Sulphuric acid acts readily on metallic oxides; converting them into sulphates. It also decomposes carbonates with the greatest ease, expelling carbon dioxide with effervescence. With the aid of heat it likewise decomposes all other salts containing acids more volatile than itself. The sulphates are a very important class of salts, many of them being extensively used in the arts. Most sulphates are soluble in water, but they are insoluble in alcohol. The barium, calcium, strontium, and lead salts are insoluble, or very slightly soluble, in water: and are formed by precipitating a soluble salt of either of those metals with sulphuric acid, or a soluble metallic sulphate. Barium sulphate is quite insoluble in water; consequently, sulphuric acid, or its soluble salts, may be detected with the greatest ease by solution of barium nitrate or chloride: a white precipitate is thereby formed which does not dissolve in nitric or hydrochloric acid.

Disulphuric or Pyrosulphuric Acid, $H_2S_2O_7$, (also called *Fuming Sulphuric Acid* and *Nordhausen Sulphuric Acid*).—This acid contains the elements of one molecule of sulphuric oxide, and one molecule of sulphuric acid, and two molecules of sulphuric acid minus one molecule of water:—



It may be obtained of definite composition and in the crystalline form by adding liquid sulphuric oxide to strong sulphuric acid in the proportions here indicated. The resulting crystals melt at 35° . This acid was originally prepared at Nordhausen, in Saxony, from an impure ferric sulphate obtained by exposing ordinary ferrous sulphate (green vitriol) to a moderate heat in contact with the air. This ferric sulphate is distilled in copper retorts arranged in a reverberatory furnace, and the distillate, consisting chiefly of sulphuric oxide, is received in a small quantity of water, or more frequently in ordinary strong sulphuric acid. A brown fuming liquid is thus obtained which agrees nearly in composition with the formula $H_2S_2O_7$, has a specific gravity of 1.9, solidifies at 10° C. to colorless crystals, and is resolved at a gentle heat into SO_2 , which distils over, and H_2SO_4 , which remains behind.

The manufacture of fuming sulphuric acid in the manner just described was first practised at Nordhausen, in Saxony, and appears to have been known since the fifteenth century: but it is now carried on almost exclusively in Bohemia. An easier and more productive method of obtaining the sulphuric oxide required for its formation is that of Messel and Squire, already described (p. 194). Fuming sulphuric acid was until lately employed only for dissolving indigo, but it is now used in very large quantities for dissolving anthraquinone for the manufacture of artificial alizarin. (See Organic Chemistry.)

The pyrosulphates, that of potassium, for example, which has the composition $K_2S_2O_7$, or $K_2SO_4.SO_3$, are prepared by the action of sulphuric oxide on the corresponding sulphates. When strongly heated, they give off sulphuric oxide, and are converted into sulphates.

Hyposulphurous Acid, H_2SO_2 (also called *Hydrosulphurous Acid*).—

This acid is formed by the action of zinc on an aqueous solution of sulphurous acid. The zinc dissolves without evolution of hydrogen, merely liberating an atom of oxygen. A yellow solution is thereby formed which possesses much greater decolorizing power than sulphurous acid itself, and quickly reduces the metals from salts of silver and mercury. This solution is, however, very unstable, and quickly loses its bleaching power. A more definite product is obtained by immersing clippings of zinc in a concentrated solution of acid sodium sulphite, $NaHSO_3$, contained in a sealed vessel, whereby sodium hypsulphite, Na_2SO_2 , and zinc-sodium sulphite, $Na_2Zn(SO_3)_2$, are produced, the latter crystallizing out. To isolate the hypsulphite, the liquid is decanted, after about half an hour, into a flask three-fourths filled with strong alcohol, and the flask is sealed. A crystalline precipitate immediately forms, consisting for the most part of zinc-sodium sulphite, while nearly all the hypsulphite remains dissolved in the alcohol. The solution, decanted into a flask quite filled with it, well closed, and left in a cool place, solidifies in a few hours to a mass of slender, colorless needles, consisting of sodium hypsulphite, which must be quickly pressed between folds of linen, and dried in a vacuum, as it becomes very hot if exposed to the air in the moist state; when dry, however, it is not affected by oxygen. This salt is very soluble in water, soluble also in dilute alcohol, the solutions exhibiting all the bleaching and reducing properties above described. The crystals when

exposed to the air are completely converted into acid sodium sulphite, NaHSO_3 . By heating them with oxalic acid, hyposulphurous acid is obtained, as a deep orange-colored strongly bleaching liquid, which quickly decomposes, becoming colorless, and depositing sulphur.*

Thiosulphuric Acid, $\text{H}_2\text{S}_2\text{O}_3$ (formerly called *Hyposulphurous Acid*).—By digesting sulphur with a solution of potassium or sodium sulphite, a portion of that substance is dissolved, and the liquid, by slow evaporation, furnishes crystals of thiosulphate: $\text{Na}_2\text{SO}_3 + \text{S} = \text{Na}_2\text{S}_2\text{O}_3$. The acid itself is scarcely known, for it cannot be isolated; when hydrochloric acid is added to a solution of a thiosulphate, the acid of the latter is almost instantly resolved into sulphur, which precipitates, and sulphurous acid, easily recognized by its odor. In a very dilute solution, however, it appears to remain undecomposed for some time. The alkaline thiosulphates readily dissolve certain salts of silver, as the chloride, which are insoluble in water—a property which has conferred upon them a considerable share of importance in relation to the art of photography. They are also much used as antichlores for removing the last traces of chlorine from bleached goods.

Seleniosulphuric Acid, H_2SeSO_3 .—This acid, having the composition of sulphuric acid in which 1 atom of oxygen is replaced by selenium, is formed by direct addition of selenium to sulphurous acid. When selenium is digested with a solution of neutral potassium sulphite, and the easily decomposable liquid, after being filtered from the selenium which separates on cooling and dilution with water, is left to evaporate at ordinary temperatures, there crystallizes out, first a sparingly soluble seleniferous salt in small shining prisms, afterwards a much more soluble salt, which is the chief product of the reaction, while the excess of sulphite remains in the mother-liquor.

The more soluble seleniferous salt is potassium seleniosulphate, K_2SeSO_3 . It is likewise formed, together with thiosulphate, when a solution of potassium selenide is mixed with sulphurous acid. It crystallizes readily, even from small quantities of solution, in large, very thin, six-sided tables belonging to the rhombic system, which deliquesce in moist air, and effloresce with partial loss of water over oil of vitriol. When heated, they turn brown and yield a polysulphide of potassium. Water separates selenium from them, and the filtered solution yields by evaporation crystals which again react in the same way with water, so that, by repeated crystallization, the whole of the seleniosulphate may be decomposed; the liquid then contains seleniotritionate. Acids, even sulphurous acid, throw down the whole of the selenium from the aqueous solution; barium chloride and baryta-water precipitate barium sulphite and selenium; calcium and manganese salts give rise to a similar decomposition. With ammoniacal silver solution the seleniosulphate forms a precipitate of silver selenide, together with potassium sulphate:—



The sulphites of sodium, ammonium, and magnesium react with selenium in the same manner as the potassium salt, the magnesium salt, however, very slowly. The seleniosulphates of sodium and ammonium are very unstable.

Dithionio or Hyposulphuric Acid, $\text{H}_2\text{S}_2\text{O}_4$.—This acid is prepared by suspending finely divided manganese dioxide in water artificially cooled,

* Schützenberger, *Zeitschrift für Chemie*, 1860, p. 545.

and then transmitting a stream of sulphurous acid gas; the dioxide becomes monoxide, half its oxygen converting the sulphurous into dithionous acid $MnO_2 + 2SO_2 = MnS_2O_4$. The manganese dithionous acid thus prepared is decomposed by a solution of pure barium hydrate, and the barium salt, formed, by enough sulphuric acid to precipitate the base. The solution of thionous acid may be concentrated by evaporation in a vacuum, until it acquires a density of 1.347; on further concentration, it decomposes into sulphuric and sulphurous acids. It has no odor, is very sour, and forms soluble salts with baryta, lime, and lead oxide.

Trithionous Acid, $H_2S_3O_6$.—A substance accidentally formed by Langlois, in the preparation of potassium thiosulphate, by gently heating with sulphur a solution of potassium carbonate saturated with sulphurous acid. It is also produced by the action of sulphurous oxide on potassium thiosulphate: $2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S$. Its salts bear a great resemblance to those of thiosulphuric acid, but differ completely in composition, while the acid itself is not quite so prone to change. It is obtained by decomposing the potassium salt with hydrofluosilicic acid: it may be concentrated under the receiver of the air-pump, but is gradually decomposed into sulphur, sulphurous and sulphuric acid.

Tetrathionous Acid, $H_2S_4O_6$.—This acid was discovered by Fordos and Berthollet. When iodine is added to a solution of barium thiosulphate, a large quantity of that substance is dissolved, and a clear colorless solution obtained, which, besides barium iodide, contains barium tetrathionate: $BaSO_3 + I_2 = BaI_2 + BaS_4O_6$. By suitable means, the acid can be eliminated and obtained in a state of solution. It very closely resembles thionous acid. The same acid is produced by the action of sulphurous acid on chlorine disulphide.

Pentathionous Acid, $H_2S_5O_6$.—This acid was discovered by Wackenroder, who formed it by the action of hydrogen sulphide on sulphurous acid: $5H_2SO_3 + 5H_2S = H_2S_5O_6 + 9H_2O + S_2$. It is colorless and inodorous, of acid and bitter taste, and capable of being concentrated to a considerable extent by cautious evaporation.

Under the influence of heat, it is decomposed into sulphur, sulphurous and sulphuric acids, and hydrogen sulphide. The salts of pentathionous acid are nearly all soluble. The barium salt crystallizes from alcohol in square prisms. The acid is also formed when lead dithionous is decomposed by hydrogen sulphide, and when chlorine monosulphide is heated with sulphurous acid.

Sulphur with Hydrogen.

Hydrogen Monosulphide—Sulphydric Acid; Hydrosulphuric Acid; Uncombined Hydrogen, H_2S .—There are two methods by which this important compound can be readily prepared, namely, by the action of dilute sulphuric acid upon iron monosulphide, and by the decomposition of antimony trisulphide with hydrochloric acid. The first method yields it most easily, the second in the purest state.

Iron monosulphide is put into the apparatus for hydrogen, already several times mentioned, together with water, and oil of vitriol is added by the funnel, until a copious disengagement of gas takes place. This is to be collected over tepid water. The reaction is thus explained:—



By the other plan, finely-powdered antimony trisulphide is put into a flask to which a cork and bent tube can be adapted, and strong liquid hydrochloric acid poured upon it. On the application of heat, a double interchange occurs, hydrogen sulphide and antimony trichloride being formed. The action lasts only while the heat is maintained.



Hydrogen sulphide is a colorless gas, having the odor of putrid eggs; it is most offensive when in small quantity, when a mere trace is present in the air. It is not irritant, but, on the contrary, powerfully narcotic. When set on fire, it burns with a blue flame, producing sulphurous acid when the supply of air is abundant, and depositing sulphur when the oxygen is deficient. Mixed with chlorine, it is instantly decomposed, with separation of the whole of the sulphur.

This gas has a specific gravity of 1.171 referred to air, or 17 referred to hydrogen as unity; a litre weighs 1.51991 grams.

A pressure of 17 atmospheres at 100° C. (500° F.) reduces it to the liquid form. Cold water dissolves its own volume of hydrogen sulphide, and the solution is used as a test; it is, however, somewhat prone to decomposition by the oxygen of the air, and should therefore be kept in a tightly closed bottle. Another mode of testing with hydrogen sulphide is to keep a little apparatus for generating the gas always at hand. A small bottle or flask, to which a bit of bent tube is fitted by a cork, is supplied with a little iron sulphide and water; when it is required for use, a few drops of oil of vitriol are added, and the gas is at once evolved. The experiment completed, the liquid is poured from the bottle, replaced by a little clean water, and the apparatus is again ready for use.

Fig. 127.



Potassium heated in hydrogen sulphide burns with great energy, becoming converted into sulphide, while pure hydrogen remains, equal in volume to the original gas. Taking this fact into account, and comparing the density of the gas with those of hydrogen and sulphur vapor, it appears that every volume of hydrogen sulphide contains one volume of hydrogen and half of a volume of sulphur-vapor, the whole condensed into one volume, a constitution precisely analogous to that of water-vapor. This corresponds with its composition by weight, determined by other means—namely, 16 parts sulphur and one part hydrogen.

When a mixture of 100 measures of hydrogen sulphide and 150 measures of pure oxygen is exploded by the electric spark, complete combustion ensues, and 100 measures of sulphurous oxide gas are produced.

Hydrogen sulphide is a frequent product of the putrefaction of organic matter, both animal and vegetable; it occurs also in certain mineral springs, as at Harrowgate and elsewhere. When accidentally present in the atmosphere of an apartment, it may be instantaneously destroyed by a small quantity of chlorine gas.

There are few reagents of greater value to the practical chemist than this substance: when brought in contact with many metallic solutions, it gives rise to precipitates, which are often exceedingly characteristic in appearance, and it frequently affords the means of separating metals from each other with the greatest precision and certainty. These precipitates are insoluble sulphides, formed by the mutual decomposition of the metallic oxides or chlorides and hydrogen sulphide, water or hydrochloric acid

being produced at the same time. All the metals are, in fact, precipitated, these sulphides are insoluble in water and in dilute acids.

Arsenic and cadmium solutions thus treated give bright yellow precipitates, the former soluble, the latter insoluble, in ammonium sulphide: tin-salts give a brown or a yellow precipitate, according as the metal is in the form of a stannous or a stannic salt; both soluble in ammonium sulphide. Antimony solutions give an orange-red precipitate soluble in ammonium sulphide. Copper, lead, bismuth, mercury, and silver salts give dark-brown or black precipitates, insoluble in ammonium sulphide: gold and platinum salts, black precipitates, soluble in ammonium sulphide.

Hydrogen sulphide possesses the properties of an acid: its solution in water reddens litmus-paper.

The best test for the presence of this compound is paper wetted with solution of lead acetate. This salt is blackened by the smallest trace of the gas.

Hydrogen Persulphide.—This very unstable substance is prepared by the following means:—

Equal weights of slaked lime and flowers of sulphur are boiled with 5 or 6 parts of water for half an hour, whereby a deep orange-colored solution is produced, containing among other things, calcium disulphide. This is filtered, and slowly added to an excess of dilute sulphuric acid, with constant agitation. A white precipitate of separated sulphur and calcium sulphate then makes its appearance, together with a quantity of yellow sulphur-looking matter, which collects at the bottom of the vessel: this is hydrogen persulphide.

This compound is generally regarded as a disulphide of hydrogen, H_2S_2 , analogous to the dioxide, but its great instability prevents the determination of its composition by direct analysis. Hofmann, however, by treating strychnine in alcoholic solution with ammonium sulphide containing free sulphur, has obtained an orange-red crystalline compound, $C_{21}H_{27}N_4O_7H_2S_2$, which is resolved by sulphuric acid into soluble strychnine sulphate and a yellow oily liquid resembling the persulphide of hydrogen obtained as above. Hence it might be inferred that this persulphide is really a sesquisulphide H_2S_3 ; but begins to decompose as soon as separated.* On the other hand, E. Schmidt, by treating an alcoholic solution of strychnine with sulphuretted hydrogen, has obtained a compound containing $2C_{21}H_{27}N_4O_7 \cdot 3H_2S_2$. The composition of hydrogen persulphide must therefore be regarded as still undecided.

Hydrogen persulphide dissolves phosphorus and iodine, forming a phosphorous sulphide and hydrogen iodide respectively, with evolution of sulphuretted hydrogen. With chlorine it forms hydrochloric acid and sulphur chloride, S_2Cl_2 . Bromine acts in a similar manner. Ammonia, either gaseous or in aqueous solution, decomposes it instantly, leaving sulphur in a peculiarly brittle, blistered state. It is remarkable that sulphurous acid, which rapidly decomposes hydrogen monosulphide, with separation of sulphur, has scarcely any action on the persulphide.†

Carbon and Sulphur.

Two compounds of these elements are known, viz.: the disulphide produced by the direct combination of its elements at a high temperature, and the monosulphide, produced by reduction of the disulphide.

Carbon Disulphide, or Bisulphide, CS_2 .—To prepare this compound a wide porcelain tube filled with pieces of charcoal which have been re-

* *Berichte der deutsch Chem. Gesellschaft*, 1868, p. 81.

† *Liebig's Annalen*, clxxx, 267.

‡ *W. Kemany, Chem. Soc. Journ.* 1874, 657.

gently heated to redness in a covered crucible, is fixed across a furnace in a slightly inclined position. Into the lower extremity a tolerably wide tube is secured by the aid of a cork; this tube bends downwards, and passes nearly to the bottom of a bottle filled with fragments of ice and a little water. The porcelain tube being heated to bright redness, fragments of sulphur are thrown into the open end, which is immediately afterwards stopped by a cork. The sulphur melts, and becomes converted into vapor, which at that high temperature combines with the carbon, forming an exceedingly volatile compound, which is condensed by the ice and collects at the bottom of the vessel. This is collected and redistilled at a very gentle heat in a retort connected with a good condenser.

For preparation on the large scale, a tubulated earthen retort is filled with charcoal, and the sulphur is dropped in through a porcelain tube passing through the tubulus and reaching nearly to the bottom; or the charcoal is contained in a large iron cylinder, and the sulphur introduced through a pipe fitted into the lower part.

Carbon disulphide is a transparent, colorless liquid of great refractive and dispersive power. Its density is 1.272, that of its vapor is 2.67. It boils at 42° C. (110° F.), and emits vapor of considerable elasticity at common temperatures. In its ordinary state, it has a very repulsive odor, due perhaps to the presence of small quantities of other volatile sulphur-compounds: but when these are removed by agitating the liquid with mercury till it ceases to blacken the bright surface of the metal, it is said to have a pure ethereal odor. When set on fire in the air, it burns with a blue flame, forming carbon dioxide and sulphur dioxide; and when its vapor is mixed with oxygen, it becomes explosive. Carbon disulphide, when heated with water in a sealed tube to about 153° C. (307° F.), is converted into carbon dioxide and hydrogen sulphide. In contact with nascent hydrogen (when heated with zinc and dilute sulphuric acid), it is converted into a white crystalline substance, having the composition CH_3S , crystallizing in square prisms, insoluble in water, alcohol, and ether, but soluble in carbon disulphide, subliming at 14° C. (57° F.), and decomposing at 200° C. (392° F.). Carbon disulphide freely dissolves sulphur, and by spontaneous evaporation deposits the latter in beautiful crystals; it also dissolves phosphorus, iodine, camphor, and caoutchouc, and mixes easily with oils. It is extensively used in the vulcanization of caoutchouc, and in the manufacture of gutta serena; also for extracting bitumen from mineral substances, and oil from seeds.

Carbon disulphide unites with metallic sulphides, forming salts called sulphocarbonates, which have the composition of carbonates with the oxygen replaced by sulphur.

| | |
|---------------------------|---|
| Calcium carbonate, | $\text{CaCO}_3 = \text{CaO.CO}_2$ |
| Calcium sulphocarbonate, | $\text{CaCS}_2 = \text{CaS.CO}_2$ |
| Hydrogen sulphocarbonate, | $\text{H}_2\text{CS}_2 = \text{H}_2\text{S.CO}_2$ |

By treating the ammonium salt with dilute sulphuric or hydrochloric acid, an oily acid liquid is precipitated, consisting of hydrogen sulphocarbonate, or sulphocarbonic acid.

Carbon Monosulphide, CS , recently discovered by Sidot,* is obtained by exposing the disulphide in sealed tubes for a considerable time to direct sunshine. It is then precipitated as a brown powder, which may be purified by distilling off the undecomposed disulphide, and washing the residual mixture of monosulphide and free sulphur with pure disulphide till all the free sulphur is removed. It is a maroon-colored powder, with-

* *Comptes Rendus*, lxxxv. 82.

out taste or smell, and having a specific gravity of 1.66. It is insoluble in water, alcohol, turpentine-oil and benzine, slightly soluble at the boiling heat in carbon disulphide and in ether. It dissolves also in caustic potash and in boiling nitric acid; the strongest nitric acid ignites it. At about 200°C . (392°F .) it is resolved into its elements, a small quantity of the disulphide being formed at the same time.

According to S. Kern,* carbon monosulphide is also formed by the prolonged action of iron wire on the disulphide in sealed tubes.

Carbon Oxy sulphide, COS .—This compound, discovered by Than, is produced by direct combination when carbon monoxide mixed with sulphur-vapor is passed through a red-hot porcelain tube. As thus prepared it is mixed with free carbon monoxide; but on passing the gas through alcoholic potash, the oxy sulphide is alone absorbed, and may be liberated in the pure state by treating the solution with hydrochloric acid.

Carbon oxy sulphide is also produced by gently heating the disulphide with an equivalent quantity of sulphur trioxide: $\text{CS}_2 + \text{SO}_3 = \text{CSO} + \text{SO}_2 + \text{S}$; and by decomposing potassium sulphocyanate with moderately dilute acids: sulphocyanic acid HCNS is then liberated and decomposed by the water present in the manner represented by the equation—



Carbon oxy sulphide is a gas of sp. gr. 2.1046, and may easily be poured from one vessel to another. It has an aromatic odor like that of some essences, slightly also that of hydrogen sulphide, and a feebler acid reaction than carbon dioxide. At a low red heat it is partly resolved into carbon monoxide and sulphur-vapor: by a fine platinum wire ignited by the electric current, it is slowly but completely decomposed, yielding an equal volume of carbon monoxide. It burns in the air with a faint blue flame, producing carbon dioxide and sulphur dioxide; with $1\frac{1}{2}$ vol. oxygen, it forms an explosive mixture, burning with a shining bluish-white flame. It is not acted upon by chlorine or fuming nitric acid at ordinary temperatures, and does not form an explosive mixture with nitrogen dioxide.

Water absorbs about its own volume of carbon oxy sulphide, acquiring a rose-tint and afterwards a pungent taste, and decomposing it after some time. It appears to exist in some sulphur springs and in the sulphurous fumes of volcanoes. Potash-solution absorbs the gas as completely as carbon dioxide, though less quickly; the solution exhibits the reaction of metallic sulphides, and when treated with acids gives off hydrogen sulphide and carbon dioxide. Baryta water, and lime-water act in a similar manner. Neutral or acid solutions of lead, copper, cadmium, and silver salts are not precipitated by the gas, but when mixed with excess of ammonia they yield with it characteristic precipitates of metallic sulphides.†

Sulphur and Chlorine.

Three chlorides of sulphur are known, represented by the formulæ, S_2Cl_2 , SCl_2 , and SCl_4 .

The monochloride, SCl or S_2Cl_2 , which may also be regarded as a disulphide of chlorine, analogous in composition to hydrogen dioxide, is prepared by passing dry chlorine-gas into a retort in which sulphur is sublimed at a gentle heat. It then distils over, and may be collected in a receiver surrounded by cold water, and freed from excess of sulphur by

* Chemical News, xxxiii. 253.

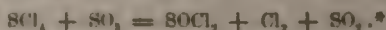
† See further, Watts's Dictionary of Chemistry, First Supplement, p. 406; Second Supplement, p. 202.

rectification. It is also produced by distilling a mixture of 1 part sulphur with 2 parts stannic chloride, or 5.5 parts mercuric chloride.

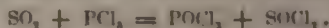
Disulphide of chlorine is a mobile reddish-yellow liquid, having a peculiar, penetrating, disagreeable odor, and fuming strongly in the air. Specific gravity = 1.637. It boils at 136° C. (276.8° F.). It dissolves in carbon disulphide, alcohol, and ether, not however without decomposition in the two latter. It dissolves sulphur in large quantities, especially when heated. When saturated with sulphur at ordinary temperatures, it forms a clear yellow liquid of specific gravity 1.7, and containing altogether 66.7 per cent. sulphur. The solution of chlorine disulphide with excess of sulphur in crude benzol, is used for vulcanizing or sulphurizing caoutchouc. It is instantly decomposed by water, with formation of hydrochloric and thiosulphuric acids, and separation of sulphur, the thio sulphuric acid in its turn decomposing into sulphur and sulphurous acid, $2S_2Cl_2 + 3H_2O = 4HCl + S_2 + H_2S_2O_3$ (or $H_2SO_3 + S$).

The dichloride, SCl_2 , is produced by passing chlorine to saturation into the preceding compound cooled by a mixture of ice and salt, and expelling the excess of chlorine by a stream of carbon dioxide. The product is a deep red liquid boiling at 164° C. (327.2° F.), and containing 30.5 per cent. of sulphur, 69.5 of chlorine, agreeing nearly with the formula SCl_2 , which requires 31.07 per cent. sulphur and 68.93 chlorine.

The tetrachloride, SCl_4 , is prepared by saturating chlorine disulphide with chlorine at -20° C. (-4° F.). The product contains 81.59 per cent. chlorine and 18.41 sulphur, the numbers calculated from the formula SCl_4 being 81.61 and 18.39. Sulphur tetrachloride is acted upon by sulphuric oxide, producing sulphurous chloride together with chlorine and sulphurous oxide: thus—

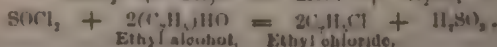


Oxychlorides.—1. *Sulphurous Chloride*, $SOCl_2$.—This compound, also called *Chloride of Thionyl*, is derived from sulphurous acid, SO_2H_2 or $SO_2.HO.HO$, by the substitution of $2Cl$ for $2H$. It is formed by the action of water, alcohols, acids, etc., on the sulphides of chlorine; but is more easily prepared by the action of phosphorus pentachloride on sulphurous oxide, or by that of phosphorus oxychloride on sulphite of calcium:—



It is separated by distillation from the fixed calcium phosphate produced simultaneously in the second, and by fractional distillation from the phosphorus oxychloride produced in the first reaction.

Sulphurous chloride is a colorless, strongly refracting liquid, which boils at 82° C. (179.6° F.). It is decomposed by water, yielding hydrochloric and sulphurous acids; and by alcohols, with formation of alcoholic chlorides and sulphurous acid, thus:—

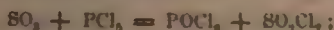


Ethyl alcohol. Ethyl chloride.

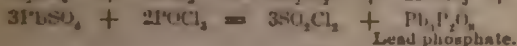
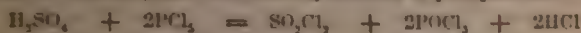
Sulphuric chloride, or *Sulphuryl chloride*, SO_2Cl_2 (also called *Chlorosulphuric acid*), is formed by prolonged exposure of a mixture of chlorine and sulphurous oxide gases to strong sunshine; also, together with phosphorus

* Respecting other reactions of the chlorides of sulphur, and especially their decomposition by heat, see Watts's Dictionary of Chemistry, Second Supplement, p. 1124.

oxychloride, by the action of phosphorus pentachloride on sulphuric oxide :—



but it is best prepared by distilling strong sulphuric acid with the pentachloride, or lead sulphate with the oxychloride of phosphorus :—

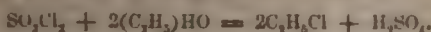


Lead phosphate.

Sulphuric chloride is a colorless fuming liquid, of specific gravity 1.66. It boils at 77°C . (170.60°F .), and may be distilled unchanged over caustic lime or baryta. When poured into water, it sinks in the form of oily drops, which gradually disappear, being converted into hydrochloric and sulphuric acids :—



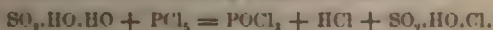
With alcohol it behaves in a similar manner, thus :—



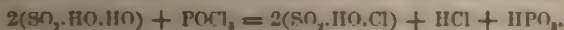
In the actual reaction, however, the sulphuric acid is converted into ethylsulphuric acid by the intervention of another atom of alcohol :—



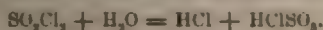
Sulphuric Hydroxychloride or **Chlorhydrate**, HClSO_3 or $\text{SO}_2\text{HO.Cl}$, Cl (also called *Chlorhydrosulphurous Acid*).—This compound, discovered by Williamson, is intermediate in composition between sulphuric acid and sulphuric chloride, is derived from sulphuric acid, SO_2H_2 or $\text{SO}_2\text{HO.HO}$, by the substitution of 1Cl for 1HO. It is the first product of the action of phosphorus pentachloride on strong sulphuric acid :—



As thus prepared it is mixed with sulphuric chloride; but it may be obtained pure by treating sulphuric acid with phosphorus oxychloride, hydrochloric acid and metaphosphoric acid being produced at the same time :—

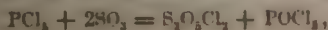


It is also formed by the action of water on sulphuric chloride :

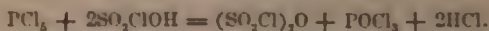


Sulphuric hydroxychloride is a colorless liquid, which boils at about 150°C . (302°F .), being at the same time partially resolved into sulphuric acid and sulphuric chloride : $2\text{HClSO}_3 = \text{H}_2\text{SO}_4 + \text{Cl}_2\text{SO}_2$. When poured into water, it sinks to the bottom and gradually dissolves, with formation of hydrochloric and sulphuric acids. It has decided acid properties, and forms definite salts in which its hydrogen is replaced by metals. Thus it dissolves sodium chloride at a gentle heat, with evolution of hydrochloric acid, and formation of the salt NaClSO_3 .

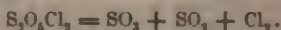
Peroxyulphuric Chloride, $\text{S}_2\text{O}_5\text{Cl}_2$ or $(\text{SO}_2\text{Cl})_2\text{O}$.—This compound is formed on heating together phosphorus pentachloride and sulphuric oxide :—



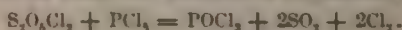
and by the action of phosphorus pentachloride on sulphuric hydroxychloride:—



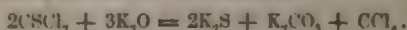
It is a colorless oily liquid of sp. gr. 1.819 at 18° C. (64.4° F.), boiling at 146° C. (294.8° F.). In contact with water it decomposes slowly and noiselessly, and is thus distinguished from sulphuric hydroxychloride, which is rapidly decomposed, with almost explosive violence, when thrown into water. When heated above its boiling point, it is resolved into chlorine, sulphurous oxide, and sulphuric oxide:—



When submitted to the action of phosphorus pentachloride, it yields chlorine, sulphurous oxide, and phosphorus oxychloride:—



Carbon Sulphochloride, CSCl₂.—This compound, the sulphur-analogue of carbonyl chloride or phosgene (p. 164), is produced, together with chlorine monosulphide, by the action of dry chlorine on carbon disulphide: $\text{CS}_2 + \text{Cl}_2 = \text{SCl}_2 + \text{CCl}_2$, or by passing a mixture of hydrogen sulphide and vapor of carbon tetrachloride through a red-hot tube: $\text{CCl}_4 + \text{H}_2\text{S} = 2\text{HCl} + \text{CSCl}_2$. It is a yellow liquid having a very irritating odor, not acted upon by water or acids, but decomposed by potash, yielding potassium sulphide, potassium carbonate, and carbon tetrachloride:—



Sulphur and Bromine.—Bromine dissolves sulphur, forming a brown red liquid probably containing a sulphur bromide analogous to sulphur monochloride; but it has not been obtained pure.

Sulphur and Iodine.—These elements combine when heated together, even under water. The resulting compound, S₂I₂, containing 32 parts of sulphur and 127 parts of iodine, is a blackish-gray radio-crystalline mass, resembling native antimony sulphide. It decomposes at higher temperatures, giving off iodine on exposure to the air, and is insoluble in water. By heating 254 parts of iodine with 32 parts of sulphur, a compound is obtained which smells like iodine, and is said to be a powerful remedy in skin diseases. A cinnabar-red sulphur iodide is obtained, according to Grosourd, by precipitating iodine trichloride with hydrogen sulphide.

SELENIUM.

Atomic weight, 79.4. Symbol, Se.

This is a very rare substance, much resembling sulphur in its chemical relations, and found in association with that element in some few localities, or replacing it in certain metallic combinations, as in the lead selenide of Clausthal in the Harz. To separate it, the pulverized ore is treated with hydrochloric acid to dissolve earthy carbonates, and the washed and dried residue is ignited for some time with an equal quantity of black flux (a mixture of potassium carbonate and charcoal). The selenium is thereby

converted into potassium selenide, which by treatment with boiling water is dissolved away from the oxides formed at the same time. This solution when exposed to the air absorbs oxygen, and yields the selenium as a gray deposit, which may be purified by washing, drying, and distillation.*

Selenium is a reddish-brown solid body, somewhat translucent, and having an imperfect metallic lustre. Its specific gravity, when rapidly cooled after fusion, is 4.3. At 100°C . (212°F .), or a little above, it melts, and boils. It is insoluble in water, and exhales, when heated in the air, a peculiar and disagreeable odor, which has been compared to that of decaying horse-radish: it is insoluble in alcohol, but dissolves slightly in carbon bisulphide, from which solution it crystallizes.

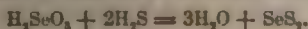
Oxides of Selenium.—Two oxides of selenium are known. The one containing the smallest proportion of oxygen is formed by the imperfect combustion of selenium in air or oxygen gas. It is a colorless gas which is the source of the peculiar horse-radish odor above mentioned. Its composition is not known.

The higher oxide, SeO_2 , called selenious oxide, is produced by burning selenium in a stream of oxygen gas; it contains 79.4 parts, by weight, of selenium, and 32 of oxygen. It is a white solid substance which absorbs water rapidly, forming a hydroxide, viz.—

| | | | | | |
|--------------------|-----------|---------|-----------|------------------|---------------|
| | Selenium. | Oxygen. | Hydrogen. | Selenious oxide. | Water. |
| Selenious acid, or | } | 79.4 | + 48 | + 2 | or 111.4 + 18 |
| Hydrogen selenite, | | | | | |

This acid, H_2SeO_3 or $\text{H}_2\text{O}.\text{SeO}_2$, analogous in composition and properties to sulphurous acid, is likewise produced by dissolving selenium in nitric or nitromuriatic acid. It is deposited from its hot aqueous solution by slow cooling in prismatic crystals like those of saltpetre; but when the solution is evaporated to dryness, the selenious acid is resolved into water and selenious oxide, which sublimes at a higher temperature.

Selenious acid is a very powerful acid, approximating to sulphuric acid in the energy of its reactions. It reddens litmus, decomposes carbonates with effervescence, and decomposes nitrates and chlorides with aid of heat. Its solution precipitates lead and silver salts, and is decomposed by hydrogen sulphide, yielding a precipitate of selenium sulphide:—



The metallic selenites resemble the sulphites. When heated with sodium carbonate in the inner blow-pipe flame, they emit the characteristic odor of selenium. They are not decomposed by boiling with hydrochloric acid.

Selenic acid, H_2SeO_4 , is a more highly oxidized acid of selenium, analogous to sulphuric acid, and containing 79.4 parts, by weight, of selenium, 64 of oxygen, and 2 of hydrogen. The corresponding anhydrous oxide is not known. Selenic acid is prepared by fusing potassium or sodium nitrate with selenium, precipitating the selenate so produced with a lead salt, and then decomposing the compound with hydrogen sulphide. The acid strongly resembles oil of vitriol; but when very much concentrated, it is decomposed, by the application of heat, into selenious acid and oxygen. The selenates bear the closest analogy to the sulphates in almost every particular. They are decomposed by boiling with hydrochloric acid, chlorine being evolved and a salt of selenious acid being produced.

Hydrogen Selenide; Selenhydric Acid; Seleniatted Hydrogen, H_2Se .—This substance is produced by the action of dilute sulphuric acid upon

* For further details, and for other methods, see *Omellin's Handbook of Chemistry*, English Edition, vol. II. p. 223.

selenide of potassium or iron. It very much resembles sulphuretted hydrogen, being a colorless gas, freely soluble in water, and decomposing metallic solutions like that substance: insoluble selenites are produced. This gas is said to act very powerfully upon the lining membrane of the nose, exciting catarrhal symptoms, and destroying the sense of smell. It contains 79.4 parts selenium and 2 parts hydrogen.

TELLURIUM.

Atomic weight, 128. Symbol, Te.

This element possesses many of the characters of a metal, but it bears so close a resemblance to selenium, both in its physical properties and its chemical relations, that it is most appropriately placed in the same group with that body. Tellurium is found in a few scarce minerals, in association with gold, silver, lead, and bismuth, apparently replacing sulphur, and is most easily extracted from the bismuth sulpho-telluride of Chemnitz in Hungary. The finely-powdered ore is mixed with an equal weight of dry sodium carbonate, the mixture made into a paste with oil, and heated to whiteness in a closely covered crucible. Sodium telluride and sulphide are thereby produced, and metallic bismuth is set free. The fused mass is dissolved in water, and the solution freely exposed to the air, when the sodium and sulphur oxidize to sodium hydrate and thiosulphate, while the tellurium separates in the metallic state.

Tellurium has the color and lustre of silver; by fusion and slow cooling it may be made to exhibit the form of rhombohedral crystals similar to those of antimony and arsenic. It is brittle, and a comparatively bad conductor of heat and electricity: it has a density of 6.25, melts at a little below a red-heat, and volatilizes at a higher temperature. Tellurium burns when heated in the air, and is oxidized by nitric acid.

Tellurium forms two oxides, analogous in composition to the oxides of sulphur, and likewise forming acids by combination with water.

| | | Composition by weight. | | | | |
|------------------|--------------------------|------------------------|------------|---------|----|----|
| | Formula. | Hydrogen. | Tellurium. | Oxygen. | | |
| Tellurous oxide, | TeO_2 | | 128 | + | 32 | |
| acid, | H_2TeO_4 | 2 | + | 128 | + | 48 |
| Telluric oxide, | TeO_3 | | 128 | + | 48 | |
| acid, | H_2TeO_6 | 2 | + | 128 | + | 64 |

Tellurous Oxide may be prepared by heating the precipitated acid to low redness. It also separates in semi-crystalline grains from the aqueous solution of the acid when gently heated; more abundantly and in well-defined octahedrons from the solution of tellurous acid in nitric acid. It is fusible and volatile, slightly soluble in water, but does not reddens litmus. When fused with alkaline hydroxides or carbonates, it forms tellurites.

Tellurous Acid is best obtained by decomposing tellurium tetrachloride with water. It may also be prepared by dissolving tellurium in nitric acid of sp. gr. 1.25, and pouring the solution, after a few minutes, into a large quantity of water. By either process it is obtained as a somewhat bulky precipitate, which, when dried over oil of vitriol, appears as a light,

white, earthy mass, having a bitter metallic taste. It is slightly soluble in water, more easily soluble in alkalis and acids, the nitric acid solution alone being unstable. Sulphurous acid, zinc, phosphorus, and other reducing agents, precipitate metallic tellurium from the acidified solution of tellurous acid. Like selenious acid, it is decomposed by hydrogen sulphide and alkaline hydrosulphides, with formation of a dark brown tellurium sulphide, which dissolves readily in excess of alkaline hydrosulphide, forming a sulfo-tellurite.

Tellurous acid is a hydroxide in which the acid and basic tendencies are nearly balanced; in other words, the tellurium of the compound can replace the hydrogen of an acid to form tellurous salts, and the hydrogen of the compound can be replaced by the basylous metals, to form metallic tellurites.

TELLURIUM SALTS.

| | |
|-------------------------------------|-----------|
| $\text{Te}(\text{SO}_3)_2$ | Sulphate. |
| $\text{Te}(\text{NO}_3)_4$ | Nitrate. |
| $\text{Te}(\text{C}_2\text{O}_4)_2$ | Oxalate. |
| TeCl_4 | Chloride. |

TELLURITES.

| | |
|--------------------------------------|-----------------------------------|
| H_2TeO_3 | Hydrogen tellurite. |
| K_2TeO_3 | Potassium tellurite. |
| HKTeO_3 | Hydrogen and potassium tellurite. |
| $\text{H}_3\text{K}(\text{TeO}_3)_2$ | Trihydrotopotassic tellurite. |

The tellurites of potassium, sodium, barium, strontium, and calcium, are formed by fusing tellurous oxide or acid, with the carbonates of the several metals in the required proportions. These tellurites are all more or less soluble in water. The tellurites of the other metals, which are insoluble, are obtained by precipitation.

Telluric Oxide and Acid.—Equal parts of tellurous oxide and sodium carbonate are fused, and the product is dissolved in water; a little sodium hydrate is added, and a stream of chlorine passed through the solution. The liquid is next saturated with ammonia, and mixed with solution of barium chloride, by which a white insoluble precipitate of barium tellurate is thrown down. This is washed and digested with a quarter its weight of sulphuric acid, and diluted with water. The filtered solution gives, on evaporation in the air, large crystals of telluric acid, which have the composition, $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$.

Crystallized telluric acid is freely, although slowly, soluble in water: it has a metallic taste, and reddens litmus-paper. The crystals give off their water of crystallization at 100° , and the remaining acid, H_2TeO_4 , when strongly heated, gives off more water, and yields the anhydrous oxide, TeO_2 , which is then insoluble in water, and even in a boiling alkaline liquid. At the temperature of ignition, telluric oxide loses oxygen, and passes into tellurous oxide.

The tellurates of the alkali-metals are soluble in water, and are prepared by dissolving the required quantities of telluric acid and an alkaline carbonate in hot water. The other tellurates are insoluble, and are obtained by precipitation.

The composition of the alkaline tellurates is exhibited by the following formulae:—

| | | | |
|---|---|---|---|
| Neutral or Bipotassic tellurate | } | K_2TeO_4 | or $\text{K}_2\text{O} \cdot \text{TeO}_3$ |
| Acid or Hydro-potassic tellurate | | HKTeO_4 | or $\text{H}_2\text{O} \cdot \text{K}_2\text{O} \cdot 2\text{TeO}_3$ |
| Quadraacid or Trihydro-potassic tellurate | } | $\text{HKTeO}_4 \cdot \text{H}_2\text{TeO}_4$ | or $3\text{H}_2\text{O} \cdot \text{K}_2\text{O} \cdot 4\text{TeO}_3$ |
| Anhydrous Quadritellurate | | $\text{K}_2\text{TeO}_4 \cdot 3\text{TeO}_2$ | or $\text{K}_2\text{O} \cdot 4\text{TeO}_3$ |

Tellurium Sulphides.—Tellurium forms two sulphides, TeS_2 and TeS_3 , analogous in composition to the oxides; they are formed by the action of hydrogen sulphide on solutions of tellurous and telluric acid respectively. They are brown or black substances, which unite with metallic sulphides, forming salts called sulphotellurites and sulphotellurates.

Hydrogen Telluride, H_2Te .—*Tellurhydric Acid, Hydrotelluric Acid, or Telluretted Hydrogen.*—This compound is a gas, resembling sulphuretted and seleniatted hydrogen. It is prepared by the action of hydrochloric acid on zinc telluride. It dissolves in water, forming a colorless liquid, which precipitates most metals from their solutions, and deposits tellurium on exposure to the air.

Tellurium Chlorides.—Tellurium forms a dichloride, TeCl_2 , and a tetrachloride, TeCl_4 , both volatile and decomposable by excess of water, the latter being completely resolved into tellurous and hydrochloric acids: $\text{TeCl}_4 + 3\text{H}_2\text{O} = 4\text{HCl} + \text{H}_2\text{TeO}_3$.

The tetrachloride unites with the chlorides of the alkali-metals, to form crystallizable double salts.

The bromides and iodides of tellurium correspond with the chlorides in properties and composition.

Compounds of the halogen-acids with tellurous oxide are also known. When this oxide is exposed to the action of gaseous hydrogen bromide in a vessel cooled to -14° , the compound $\text{TeO}_2 \cdot 3\text{HBr}$ is formed in groups of small nearly black scales resembling iodine. At 40° this compound gives off HBr , and is reduced to $\text{TeO}_2 \cdot 2\text{HBr}$, which, when heated to 300° , is resolved into water and a yellow oxybromide: $\text{TeO}_2 \cdot 2\text{HBr} = \text{H}_2\text{O} + \text{TeOBr}_2$; and at a still higher temperature this oxybromide is decomposed into the tetrabromide and tellurous oxide: $2\text{TeOBr}_2 = \text{TeBr}_4 + \text{TeO}_2$. The tetrabromide passes off in black vapors, and crystallizes on cooling in dark brown needles.

Tellurous oxide is decomposed by hydriodic acid at ordinary temperatures, but absorbs it at -15° , forming a compound which decomposes as the temperature rises. Tellurous oxide likewise absorbs anhydrous hydrofluoric acid.

BORON.

Atomic weight, 11. Symbol, B.

This element, the basis of boric or boracic acid, is prepared by heating the double fluoride of boron and potassium with metallic potassium in a small iron vessel, and washing out the soluble salts with water. It is a dull, greenish-brown powder, which burns in the air when heated, producing boric oxide. Nitric acid, alkalies in the fused state, chlorine, and other agents, attack it readily.*

Boric Oxide and Acid.—There is but one oxide of boron, namely, boric oxide, B_2O_3 , containing 22 parts of boron and 48 of oxygen. It unites with water and metallic oxides, forming boric acid and metallic borates.

* Wöhler and Berzeli, in 1836, by fusing boric oxide with aluminium, obtained very hard octohedral crystals and a graphite-like substance, which they regarded as modifications of boron analogous to the diamond and graphite varieties of carbon; but subsequent observations have shown that both these substances are compounds of boron and aluminium. (See ALUMINIUM.)

Boric or Boracic Acid, or Hydrogen Borate, H_3BO_3 or $3H_2O.B_2O_3$, contains 11 parts boron, 48 oxygen, and 3 hydrogen, or 70 parts boric oxide, and 1 water. It is found in solution in the water of the hot volcanic lagoons of Tuscany, whence a large supply is at present derived. It is also easily made by decomposing with sulphuric acid a hot solution of borax, which is an acid borate of sodium, occurring abundantly in certain salt lakes of India, Thibet, and other parts of Asia.

Boric acid crystallizes in transparent colorless plates, soluble in about 2 parts of cold water, and in a much smaller quantity at the boiling heat. The acid has but little taste, and feebly affects vegetable colors. When heated, it loses water, and melts to a glassy transparent mass of anhydrous boric oxide, which dissolves many metallic oxides with great ease. The crystals dissolve in alcohol, and the solution burns with a green flame.

Glassy boric oxide in a state of fusion requires for its dissipation in vapor a very intense and long-continued heat; the aqueous solution cannot, however, be evaporated without very appreciable loss by volatilization; hence it is probable that the acid is far more volatile than the anhydrous oxide.

Boron Nitride, BN.—This compound, containing 11 parts of boron and 14 of nitrogen, is produced by heating boric oxide with metallic granules, or by heating to bright redness a mixture of sal-ammoniac and pure anhydrous borax, or sodium baborate, $Na_2O.2B_2O_3$:—



It is a white amorphous powder, insoluble in water, infusible, and non-volatile. When heated in a current of steam, it yields ammonia and boric oxide: $2BN + 3H_2O = 2NH_3 + B_2O_3$, and likewise gives off a large quantity of ammonia when fused with potash.

Boron Chloride, BCl_3 , was formerly believed to be a permanent gas; but recent researches have proved that it is a liquid, boiling at $17^\circ C.$ ($62.6^\circ F.$), according to Wöhler and Deville, at $18.23^\circ C.$ ($64.80^\circ F.$) under a pressure of 2760 millimetres (Regnault). It is decomposed by water, with production of boric and hydrochloric acids, and fuming strongly in the air. It is most easily obtained by exposing to the action of dry chlorine, at a very high temperature, an intimate mixture of glassy boric oxide and charcoal.

There is also a *Boron Bromide* of similar constitution.

Boron Fluoride, BF_3 , is obtained by heating in a glass flask or retort 1 part of vitrified boric oxide, 2 of fluor-spar, and 12 of oil of vitriol. It is a transparent gas, very soluble in water, very heavy, and forming dense fumes in the air.

SILICON or SILICIUM.

Atomic weight, 28. Symbol, Si.

This element in union with oxygen constitutes silica or the earth of flint, in which form it enters largely into the composition of many of the rocks and mineral masses of which the surface of the earth is composed.

The following process yields silicon most readily: The double fluoride of silicon and potassium is heated in a glass tube with nearly its own weight of metallic potassium; violent reaction ensues, and silicon is set free. When cold, the contents of the tube are put into cold water, which removes the saline matter and any residual potassium, and leaves the silicon untouched. So prepared, silicon is a dark-brown powder, destitute of lustre. Heated in the air, it burns, and becomes superficially converted into silica. It is also acted upon by sulphur and by chlorine. When silicon is strongly heated in a covered crucible, its properties are greatly changed; it becomes darker in color, denser, and incombustible, refusing to burn even when heated by the flame of the oxy-hydrogen blowpipe.

Silicon, like carbon, is capable of existing in three different modifications. The modification above mentioned corresponds with the amorphous variety of carbon (lamp-black). The researches of Wöhler and Deville have established the existence of modifications corresponding with the diamond, and with the graphite variety of carbon. The diamond modification of silicon is most readily obtained by introducing into a red-hot crucible a mixture of 3 parts of potassium silico-fluoride, 1 part of sodium in small fragments, and 1 part of granulated zinc, and heating to perfect fusion. On slowly cooling, there is formed a button of zinc, covered and interspersed with needle-shaped crystals consisting of octohedrons joined in the direction of the axis. This crystallized silicon, which may be readily freed from zinc by treatment with acids, resembles crystallized hematite in color and appearance: it scratches glass, and fuses at a temperature approaching the melting point of cast-iron. The graphite modification of silicon is prepared by fusing, in a Hessian crucible, 5 parts of soluble glass (potassium silicate), 10 parts of cryolite (sodium and aluminium fluoride), and 1 part of aluminium. On treating the resulting button of aluminium with hydrochloric acid, the silicon remains in the form of scaly crystals, resembling graphite, but of somewhat brighter color, scratching glass, like the previous modification. It is infusible. Its specific gravity is 2.49.

Silica, or Silicic Oxide, SiO_2 .—This is the only known oxide; it contains 28 parts silicon and 32 parts oxygen. Colorless transparent rock-crystal consists of silica very nearly pure; common quartz agate, chalcedony, flint, and several other minerals, are also chiefly composed of this substance.

Fig. 128.



The following experiment furnishes silica in a state of complete purity, and at the same time exhibits one of the most remarkable properties of silicon, namely, its attraction for fluorine. A mixture of equal parts of fluor-spar and glass, both finely powdered, is introduced into a glass flask, with a quantity of oil of vitriol. A tolerably wide bent tube, fitted to the flask by a cork, passes to the bottom of a glass jar (fig. 128), into which enough mercury is poured to cover the extremity of the tube. The jar is then half filled with water, and heat is applied to the flask.

The first effect is the disengagement of hydrofluoric acid: this substance, however, finding itself in contact with the silica of the powdered glass, undergoes decomposition, water and silicon fluoride being produced. The latter is a permanent gas, which escapes from the flask by the bent tube. By contact with a large quantity of water, it is in turn decomposed, yielding silica, which separates in a beautiful gelatinous condition, and an acid liquid, which is a double fluoride of silicon and hydrogen, $4\text{HF} \cdot \text{SiF}_6$, commonly called hydrofluosilicic or silico-fluoric acid, thus

(1) Reaction of hydrofluoric acid with silica :—



(2) Decomposition of silicon fluoride by water :—



The silica may be collected on a cloth-filter, well washed, dried, and heated to redness to expel water. The acid liquid is kept as a test for barium and potassium, with which it forms nearly insoluble precipitates, the double fluoride of silicon and potassium being used, as was stated, in the preparation of silicon.

Silicon fluoride, SiF_4 , instead of being condensed into water, may be collected over mercury; it is a permanent gas, destitute of color, and very heavy. Admitted into the air, it condenses the moisture of the latter, giving rise to a thick white cloud. It is important, in the experiment above described, to keep the end of the delivery-tube from touching the water of the jar, otherwise it almost instantly becomes stopped: the mercury effects this object.

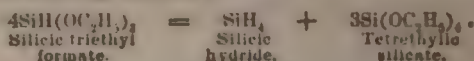
Pure silica may also be prepared by another method, which is very instructive, inasmuch as it is the basis of the proceeding adopted in the analysis of all siliceous minerals. Powdered rock-crystal or fine sand is mixed with about three times its weight of dry sodium carbonate, and the mixture fused in a platinum crucible. When cold, the glassy mass is boiled with water, by which it is softened, and almost entirely dissolved. An excess of hydrochloric acid is then added to the filtered liquid, and the whole evaporated to complete dryness. By this treatment the gelatinous silica thrown down by the acid becomes completely insoluble, and remains behind when the dry saline mass is treated with acidulated water, by which the alkaline salts, alumina, ferric oxide, lime and many other bodies which may happen to be present, are removed. The silica is washed, dried, and heated to redness.

The most prominent characters of silica are the following: It is a very fine, white, tasteless powder, having a density of about 2.66, fusible only by the oxy-hydrogen blow-pipe. When once dried it is not sensibly soluble in water or dilute acids (with the exception of hydrofluoric acid). But, on adding hydrochloric acid to a very dilute solution of potassium silicate, the liberated silica remains in solution. From this mixed solution of silica and potassium chloride, the latter may be separated by diffusion (comp. p. 144), whereby a moderately concentrated solution of silica in water is obtained. This solution has a distinctly acid reaction: it prevents, however, but little stability. When kept for some time, it gelatinizes, the silica separating in the insoluble modification. The same effect is produced by the addition of a few drops of sulphuric or nitric acid, or of a solution of salt.

Silica is essentially an acid oxide, forming salts with basic metallic oxides, and decomposing all salts of volatile acids when heated with them. In strong alkaline liquids it is freely soluble. When heated with bases, especially those which are capable of undergoing fusion, it unites with them and forms salts, which are sometimes soluble in water, as in the case of the potassium and sodium silicates, when the proportion of base is considerable. Common glass is a mixture of several silicates, in which the reverse of this happens, the silica being in excess. Even glass, however, is slowly acted upon by water. Finely divided silica is highly useful in the manufacture of porcelain.

Silicon Hydride, or *Silicated Hydrogen*, was discovered by Buff and Winter, who obtained it by passing an electric current through a solution

of sodium chloride, the positive pole employed consisting of aluminium containing silicon. More recently, Wöhler and Martius produced this gas by treating magnesium containing silicon with hydrochloric acid. Both methods yield silicic hydride mixed with free hydrogen. Frasel and Ladenburg, however, by decomposing silicic triethyl-formate (see SILICON ETHERS) in contact with sodium, have obtained it pure, and shown that it consists of 28 parts by weight of silicon and 4 parts of hydrogen, answering to the formula SiH_4 . The reaction by which it is produced is represented by the following equation:—



Silicon hydride is a colorless gas. In the impure state, as obtained by the two processes above given, it takes fire spontaneously on coming in contact with the air, and burns with a white flame, evolving clouds of silica. Pure silicic hydride, however, does not ignite spontaneously under the ordinary atmospheric pressure; but on passing a bubble of air into the rarefied gas standing over mercury, it takes fire, and yields a deposit of amorphous silicon mixed with silica. On passing silicic hydride through a red-hot tube, it is decomposed, silicon being deposited.

COMPOUNDS OF SILICON AND CHLORINE.—Silicon unites directly with chlorine, forming a tetrachloride, SiCl_4 . This compound is obtained by mixing finely divided silica with charcoal powder and oil, strongly heating the mixture in a covered crucible, and then exposing the mass so obtained, in a porcelain tube heated to full redness, to the action of perfectly dry chlorine gas. A good condensing arrangement, supplied with ice-cold water, must be connected with the porcelain tube. The product is a colorless and very volatile liquid, boiling at 50°C , of pungent, suffocating odor. In contact with water, it yields hydrochloric acid and gelatinous silica.

When hydrochloric acid gas is passed over crystallized silicon heated to a temperature below redness, a very volatile inflammable liquid is obtained, which, when purified by distillation, has the composition of *silicic hydrotrichloride*, SiHCl_3 , containing 28 parts silicon, 1 hydrogen, and 106.5 chlorine. This compound is decomposed by water, forming a white oxygenated body, probably *silicon hydrotrioxide*, $\text{Si}_2\text{H}_2\text{O}_3$, which, by prolonged contact with water is further decomposed, with evolution of hydrogen and formation of silica.

A mixture of silicic hydrotrichloride and bromine heated to 100° in a closed vessel becomes dark colored, and is converted into the *bromotrichloride*, SiBrCl_3 .

Silicon tetrabromide, SiBr_4 , obtained like the tetrachloride, resembles that compound, but is less volatile.

Silicon Fluoride, SiF_4 , has been already described (p. 213).

PHOSPHORUS.

Atomic weight, 31. Symbol, P.

Phosphorus in the state of phosphoric acid is contained in the ancient unstratified rocks and in lavas of modern origin. As these disintegrate and crumble down into fertile soil, the phosphates pass into the organism

plants, and ultimately into the bodies of the animals to which the plants are for food. The earthy phosphates play a very important part in the structure of the animal frame, by communicating stiffness and inflexibility to the bony skeleton.

Phosphorus was discovered in 1669 by Brandt, of Hamburg, who prepared it from urine. The following is an outline of the process now adopted. Thoroughly calcined bones are reduced to powder, and mixed with two-thirds of their weight of sulphuric acid diluted with a considerable quantity of water: this mixture, after standing for some hours, is filtered, and the nearly insoluble calcium sulphate is washed. The liquid is then evaporated to a syrupy consistence, mixed with charcoal powder, and the desiccation is completed in an iron vessel exposed to a high temperature. When quite dry, it is transferred to a stoneware retort to which a bent tube is luted, dipping a little way into the water contained in a receiver. A narrow tube serves to give issue to the gases, which are conveyed to a chimney. This manufacture is now conducted on a very large scale, the consumption of phosphorus, for the apparently trifling purpose of instantaneous-light matches, being something prodigious.

Phosphorus, when pure, very much resembles in appearance imperfectly fused wax, and is soft and flexible at common temperatures. Its density is 1.77, and that of its vapor 4.35, air being taken, or 62 referred to hydrogen as unity. It melts at 44° C. (111° F.), and boils at 280° C. (536° F.).

On slowly cooling melted phosphorus, six-sided dodecahedrons are sometimes obtained. It is insoluble in water, and is usually kept immersed in that liquid, but dissolves in carbon disulphide, native naphtha, and especially in carbon tetrachloride. When set on fire in the air, it burns with a bright flame, generating phosphoric oxide. Phosphorus is exceedingly inflammable; it sometimes takes fire by the heat of the hand, and demands great care in its management: a blow or a hot rod will very often kindle it. A stick of phosphorus held in the air always appears to emit a whitish smoke, which in the dark is luminous. This effect is chiefly due to a slow combustion which the phosphorus undergoes by the action of the air, and upon it depends one of the methods employed for the analysis of air, as already described. It is singular that the slow oxidation of phosphorus may be entirely prevented by the presence of a small quantity of olefiant gas, or the vapor of ether, or some essential oil; phosphorus may even be distilled in an atmosphere containing vapor of oil of turpentine in considerable quantity. Neither does the action go on in pure nitrogen—at least, at the temperature of 15.5° C. (60° F.), which is very remarkable; but if the gas be rarefied, or diluted with nitrogen, hydrogen, or carbonic acid, oxidation is set up.

A very remarkable modification of this element is known by the name of amorphous phosphorus. It was discovered by Schrötter, and may be made by exposing common phosphorus for fifty hours to a temperature of 240° C. to 250° C. (464° to 482° F.), in an atmosphere which is unable to act chemically upon it. At this temperature, it becomes red and opaque, and insoluble in carbon bisulphide, whereby it may be separated from ordinary phosphorus. It may be obtained in compact masses when common phosphorus is kept for a week at a constant high temperature. It is a coherent, reddish-brown, infusible substance, of specific gravity between 2.089 and 2.106. It does not become luminous in the

Fig. 120.



dark until its temperature is raised to about 200°C . (392°F .), nor has it any tendency to combine with the oxygen of the air. When heated to 260°C . (500°F .), it is reconverted into ordinary phosphorus.

When phosphorus is melted beneath the surface of hot water, and a stream of oxygen gas forced upon it from a bladder, combustion ensues, and the phosphorus is converted in great part into a brick-red powder, which was formerly believed to be a peculiar oxide of phosphorus, but Schröter has shown that it is a mixture, consisting chiefly of amorphous phosphorus.

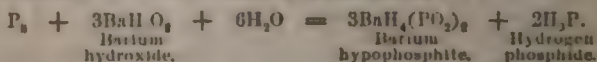
Compounds of Phosphorus and Oxygen.

There are two definite oxides of phosphorus, in which the quantities of oxygen united with the same quantity of phosphorus are to one another as 3 to 5, viz. :—

| | Formula. | Composition by weight | | |
|---|------------------------|-----------------------|---|---------|
| | | Phosphorus. | | Oxygen. |
| Phosphorus trioxide, or }
Phosphorous oxide, } | P_2O_3 | 62 | + | 48 |
| Phosphorus Pentoxide, }
or Phosphoric oxide, } | P_2O_5 | 62 | + | 80 |

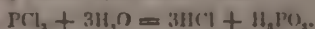
Both these acid oxides, uniting with water and metallic oxides to form salts, called phosphites and phosphates respectively; the hydrogen salts being also called phosphorous and phosphoric acid. There is also another oxygen acid of phosphorus, containing a smaller proportion of oxygen, called hypophosphorous acid, to which there is no corresponding anhydrous oxide.

Hypophosphorous Acid, H_3PO_2 .—When phosphorus is boiled with a solution of lime or baryta, water is decomposed, giving rise to phosphoretted hydrogen and hypophosphorous acid: the first escapes as gas, and the hypophosphorous acid remains as a barium salt :—



The soluble hypophosphite may be crystallized out by slow evaporation. On adding to the liquid the quantity of sulphuric acid necessary to precipitate the base, the hypophosphorous acid is obtained in solution, and may be reduced to a syrupy consistence by evaporation. The acid is very prone to absorb more oxygen, and is therefore a powerful deoxidizing agent. All its salts are soluble in water.

Phosphorous Oxide, P_2O_3 , is formed by the slow combustion of phosphorus in the air: or by burning that substance by means of a very limited supply of dry air, in which case it is anhydrous, and presents the aspect of a white powder. *Phosphorous Acid, H_3PO_3* , or $3\text{H}_2\text{O.P}_2\text{O}_3$, is most conveniently prepared by adding water to the trichloride of phosphorus, when mutual decomposition takes place, the oxygen of the water being transferred to the phosphorus, generating phosphorous acid, and its hydrogen to the chlorine, giving rise to hydrochloric acid :—



By evaporating the solution to the consistence of syrup, the hydrochloric acid is expelled, and the residue crystallizes on cooling.

Phosphorous acid is very deliquescent, and very prone to attract oxygen and pass into phosphoric acid. When heated in a close vessel, it is re-

and into phosphoric acid and pure phosphoretted hydrogen gas. It is composed of 110 parts of phosphorous oxide and 54 parts of water, or 31 phosphorus, 48 oxygen, and 3 hydrogen.

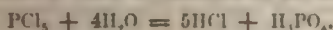
Phosphoric Oxide, P_2O_5 (also called *Anhydrous Phosphoric Acid*, or *Phosphoric Anhydride*).—When phosphorus is burned under a bell-jar by the aid of a copious supply of dry air, snow-like phosphoric oxide is produced in great quantity. This substance exhibits attraction for water, stronger even than that of sulphuric oxide; in fact sulphuric oxide may be prepared by heating strong sulphuric acid in contact with phosphoric oxide. Exposed to the air for a few moments, phosphoric oxide deliquesces and is absorbed, and when thrown into water, combines with the latter with explosive violence, and is converted into phosphoric acid. The water thus taken up cannot again be separated.

When nitric acid of moderate strength is heated in a retort with which a receiver is connected, and fragments of phosphorus are added singly, taking care to suffer the violence of the action to subside after each addition, the phosphorus is oxidized to its maximum, and converted into phosphoric acid. By distilling off the greater part of the nitric acid, transferring the residue in the retort to a platinum vessel, and then cautiously raising the heat to redness, the phosphoric acid may be obtained pure. This is the *glacial phosphoric acid* of the Pharmacopœia.

A third method of preparing phosphoric acid consists in taking the acid calcium phosphate produced by the action of sulphuric acid on bone-earth, precipitating it with a slight excess of ammonium carbonate, separating by filtration the insoluble calcium salt, and then evaporating and igniting in a platinum vessel the mixed phosphate and sulphate of ammonium. Phosphoric acid alone remains behind. The acid thus obtained is somewhat impure.

One of the most advantageous methods of preparing pure phosphoric acid on the large scale, is to burn phosphorus in a two-necked glass globe through which a current of dry air is passed: in this way the process may be carried on continuously. The phosphoric oxide obtained may be preserved in that state, or converted into hydrate or glacial acid, by addition of water and subsequent fusion in a platinum vessel.

Glacial phosphoric acid, or metaphosphoric acid, is exceedingly hygroscopic, and requires to be kept in a closely stopped bottle. It contains 142 parts of phosphoric oxide and 18 parts of water, or 31 phosphorus, 48 oxygen, and 1 hydrogen, and is represented by the formula HPO_3 , P_2O_5 , or $H_2P_2O_5$. Phosphoric oxide likewise unites with 2 and 3 molecules of water, forming the compounds $2H_2O.P_2O_5$ or $H_4P_2O_7$ and $3H_2O.P_2O_5$ or $H_6P_2O_9$, called respectively pyrophosphoric acid and orthophosphoric acid. The last is formed by oxidizing phosphorus with nitric acid, and by the action of water on phosphorus pentachloride:



The aqueous solution evaporated to a thin syrup, and left over oil of vitriol, deposits orthophosphoric acid in prismatic crystals. The same solution may be heated to $160^\circ C.$ ($320^\circ F.$) without change in the composition of the acid; but at $213^\circ C.$ ($415.4^\circ F.$) it gives off a molecule of water, and is converted into pyrophosphoric acid; and at a red-heat it gives off another molecule of water, and leaves metaphosphoric acid. Each of these acids forms a distinct class of salts, exhibiting reactions peculiar to itself. They will be described in connection with the general theory of saline compounds.

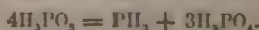
Phosphoric oxide is readily volatilized, and may be sublimed by the heat of an ordinary spirit-lamp. The acid may be fused in a platinum

crucible at a red-heat; at this temperature it evolves considerable quantities of vapor, but is still far from its boiling point. Phosphoric acid is a very powerful acid: being less volatile than sulphuric acid, it expels the latter at higher temperatures, although it is displaced by sulphuric acid at common temperatures. Its solution has an intensely sour taste, and reddens litmus-paper; it is not poisonous.

Compounds of Phosphorus and Hydrogen.

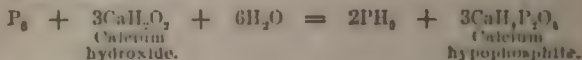
Phosphorus Trihydride.—*Phosphine.*—*Phosphoretted Hydrogen*, PH_3 .—This body is analogous in some of its chemical relations to ammoniacal gas; its alkaline properties are, however, much weaker.

It may be obtained in a state of purity by heating phosphorous acid in a small retort, the acid being then resolved into phosphoretted hydrogen and phosphoric acid:



Thus obtained, the gas has a density of 1.24. It contains 31 parts phosphorus and 3 parts hydrogen, and is so constituted that every two volumes contain 3 volumes of hydrogen and half a volume of phosphorus vapor, condensed into two volumes. It has a highly disagreeable odor of garlic, is slightly soluble in water, and burns with a brilliant white flame, forming water and phosphoric acid.

Phosphoretted hydrogen may also be produced by boiling together, in a retort of small dimensions, caustic potash or slaked lime, water, and phosphorus: the vessel should be filled to the neck, and the extremity of the latter made to dip into the water of the pneumatic trough. In the reaction which ensues, the water is decomposed, and both its elements combine with the phosphorus.



The phosphoretted hydrogen prepared by the latter process has the singular property of spontaneous inflammability when admitted into the air or into oxygen gas; with the latter, the experiment is very beautiful, but requires caution: the bubbles should be admitted singly. When kept over water for some time, the gas loses this property, without otherwise suffering any appreciable change; but if dried by calcium chloride, it may be kept unaltered for a much longer time. Paul Thénard has shown that the spontaneous combustibility of the gas arises from the presence of the vapor of a liquid hydrogen phosphide, PH_3 , which can be procured in small quantity, by conveying the gas produced by the action of water on calcium phosphide through a tube cooled by a freezing mixture. This substance forms a colorless liquid of high refractive power and very great volatility. It does not freeze at -17.8°C . (60°F). In contact with air it inflames instantly, and its vapor in very small quantity communicates spontaneous inflammability to pure phosphoretted hydrogen, and to all other combustible gases. It is decomposed by light into gaseous phosphoretted hydrogen, and a solid phosphide, P_2H_4 , which is often seen on the inside of jars containing gas which, by exposure to light, has lost the property of spontaneous inflammation. Strong acids occasion its instantaneous decomposition. It is as unstable as hydrogen dioxide. It is to be observed that pure phosphoretted hydrogen gas itself becomes spontaneously inflammable if heated to the temperature of boiling water.

Phosphoretted hydrogen decomposes several metallic solutions, giving rise to precipitates of insoluble phosphides. With hydriodic acid it forms a crystalline compound, PH_3I , somewhat resembling red ammoniac.

Compounds of Phosphorus with Chlorine.

Phosphorus forms two chlorides, analogous in composition to the oxides, the quantities of chlorine combined with the same quantity of phosphorus being in the proportion of 3 to 5.

Phosphorus Trichloride, or Phosphorous Chloride, PCl_3 , is prepared in the same manner as sulphur dichloride, by gently heating phosphorus in dry chlorine gas, the phosphorus being in excess; or by passing the vapor of phosphorus over fragments of calomel (mercurous chloride) contained in a glass tube, and strongly heated. It is a thin, colorless liquid, which fumes in the air, and has a powerful and offensive odor. Its specific gravity is 1.45. Thrown into water, it sinks to the bottom, and is slowly decomposed, yielding phosphorous acid and hydrochloric acid: $\text{PCl}_3 + 3\text{H}_2\text{O} = 3\text{HCl} + \text{H}_3\text{PO}_3$.

Phosphorus Pentachloride, or Phosphoric Chloride, PCl_5 , is formed when phosphorus is burned in excess of chlorine. Pieces of phosphorus are introduced into a large tubulated retort, which is then filled with dry chlorine gas. The phosphorus takes fire, and burns with a pale flame, forming a white volatile crystalline sublimate, which is the pentachloride. It may be obtained in larger quantity by passing a stream of dry chlorine gas into the liquid trichloride, which becomes gradually converted into a solid crystalline mass. Phosphorus pentachloride is decomposed by water, yielding phosphoric and hydrochloric acids: $\text{PCl}_5 + 5\text{H}_2\text{O} = 5\text{HCl} + \text{H}_3\text{PO}_4$.

Phosphorus Oxychloride, POCl_3 , is produced, together with hydrochloric acid, when phosphorus pentachloride is heated with a quantity of water sufficient to convert it into phosphoric acid. It may also be prepared by distilling the pentachloride with dehydrated oxalic acid, or by distilling a mixture of phosphorus pentachloride and phosphoric oxide. It is a colorless liquid, of sp. gr. 1.7, possessing a very pungent odor, boiling at 120° , readily decomposed by water into hydrochloric and phosphoric acids.

A *sulphochloride* of analogous composition is produced by the action of carbon disulphide on the pentachloride. It is a colorless oily liquid, decomposed by water.

Two bromides of phosphorus, an oxybromide, and a sulphobromide, are known, corresponding in composition and properties with the chlorine compounds, and obtained by similar processes.

Phosphorus forms also two iodides, PI_2 and PI_3 . Both are obtained by heating phosphorus and iodine together in carbon bisulphide, and cooling the liquid till crystals are deposited. Whatever proportions of iodine and phosphorus may be used, these two compounds always crystallize out, mixed with excess either of iodine or of phosphorus.

The *di-iodide* melts at $110^\circ \text{C. (230^\circ \text{F.})}$, forming a red liquid which continues to a light red solid. The *tri-iodide* melts at $55^\circ \text{C. (131^\circ \text{F.})}$, and crystallizes on cooling in well-defined prisms. Both are decomposed by water, yielding hydriodic and phosphorous acids, the di-iodide also depositing yellow flakes of phosphorus.

Compounds of Phosphorus with Sulphur and Selenium.

Sulphides.—When ordinary phosphorus and sulphur are heated together in the dry state, or melted together under water, combination

or 3 parts hydrogen with 14 parts nitrogen. When potassium is heated in ammonia gas, a compound called potassamine is formed, in which one-third of the hydrogen is replaced by potassium. Another compound, called tripotassamine, is also known, consisting of ammonia in which the whole of the hydrogen is replaced by an equivalent quantity of potassium.

There is also a large class of compounds derived from ammonia in like manner by the replacement of $\frac{1}{3}$, $\frac{2}{3}$, or the whole of the hydrogen by equivalent quantities of certain groups of elements called *compound radicles* (see page 238). Hence, by reasoning similar to that which was above applied to water, it is inferred that the molecule of ammonia contains 3 atoms of hydrogen, and that the atomic weight of nitrogen is 14. Moreover, in certain organic compounds, this quantity of nitrogen may be substituted for 3 parts of hydrogen, or $\frac{1}{3}$ nitrogen for 1 hydrogen; consequently the atomic weight of nitrogen is three times its equivalent weight.

Next take the case of *marsh gas* or *methane*, a compound of 1 part hydrogen with $\frac{1}{4}$ parts carbon, or 4 of hydrogen with 12 of carbon. When this gas is mixed with chlorine, and exposed to diffuse daylight, a new compound is formed, in which one-fourth of the hydrogen belonging to the marsh gas is replaced by an equivalent quantity of chlorine; and if the chlorine is in excess, and the mixture exposed to sunshine, three other compounds are formed, in which one-half, three-fourths, and all the hydrogen, are thus replaced. The results may be thus expressed:—

| | | | | | | | | |
|---------|---|---------------------------------|---|-----------|---|-----------|---|-----------|
| | | Methane. | | | | | | |
| Carbon. | | Hydrogen. | | | | | | |
| 12 | + | 1 | + | 1 | + | 1 | + | 1 |
| | | Chloromethane. | | | | | | |
| Carbon. | | Hydrogen. | | | | | | Chlorine. |
| 12 | + | 1 | + | 1 | + | 1 | + | 35.5 |
| | | Dichloromethane. | | | | | | |
| Carbon. | | Hydrogen. | | | | Chlorine. | | |
| 12 | + | 1 | + | 1 | + | 35.5 | + | 35.5 |
| | | Trichloromethane or Chloroform. | | | | | | |
| Carb. | | Hyd. | | Chlorine. | | | | |
| 12 | + | 1 | + | 35.5 | + | 35.5 | + | 35.5 |
| | | Tetrachloromethane. | | | | | | |
| Carbon. | | Chlorine. | | | | | | |
| 12 | + | 35.5 | + | 35.5 | + | 35.5 | + | 35.5 |

Hence, by reasoning similar to the above, it is inferred that the molecule of methane contains 4 atoms of hydrogen, and that the atomic weight of carbon is 12. Moreover, as this quantity of carbon can unite with 4×35.5 parts, or 4 atoms of chlorine, it follows that the atomic weight of carbon is equal to four times its equivalent weight.

We have thus shown in three cases how the atomic weight of an element may be determined by the proportion in which equivalent substitution takes place in its compounds with hydrogen. Sulphur, selenium, and tellurium, form hydrogen-compounds exactly analogous in this respect to water, the hydrogen being replaceable by halves; their atomic weights

GENERAL LAWS OF CHEMICAL COMBINATION— ATOMIC THEORY.

Before proceeding further with the study of individual compounds, it is advisable to enter more fully into the consideration of certain general laws of chemical combination, and certain theoretical notions founded thereon, a sketch of which has already been given in the chapter on Oxygen (pp. 123-128).

The laws in question are: (1) The Law of Equivalents, according to which the replacement of elements one by another always takes place in definite proportion; (2) The Law of Multiples, according to which the several quantities of an element A which can unite with a fixed quantity of another element B , stand to one another, for the most part, in simple numerical proportions. The observation of these laws has led to the idea that the elementary bodies are made up of indivisible particles called atoms, each having a constant weight peculiar to itself, and that chemical combination takes place by the juxtaposition of these atoms, 1 to 1, 1 to 2, 1 to 3, 2 to 3, etc., a group of atoms thus united being called a molecule. This is the atomic hypothesis of Dalton.

Equivalents.—The equivalent weight of an elementary body compared with that of hydrogen, taken as unity, may, in many cases, be determined by direct substitution. Thus, when a metal dissolves in hydrochloric or sulphuric acid, the quantity of the metal which takes the place of 1 part by weight of hydrogen is its equivalent weight. In this manner it is found that the equivalent of sodium is 23, of zinc 32.6, of magnesium 12, etc. Again, many organic compounds—acetic acid, for example—are acted upon by chlorine and bromine in such a manner that 1 part of the hydrogen is removed and its place supplied by chlorine or bromine, every 1 part by weight (gram, ounce, etc.) of hydrogen thus removed being replaced by 35.5 parts of chlorine, or by 80 parts of bromine: these numbers are therefore the equivalent weights of chlorine and bromine.

When one element A unites with each of a number of others, B, C, D , etc., in one proportion only, the quantities of these latter which combine with or saturate a given quantity of A , are clearly proportional to their equivalent weights. Thus, 35.5 parts of chlorine are known to unite with 1 part of hydrogen, 23 of sodium, 39.1 of potassium, 32.6 of zinc; consequently, the numbers 23, 39.1, and 32.6 are the equivalent weights of sodium, potassium, and zinc referred to hydrogen as unity. In this manner, the equivalent weights of elements may be determined without recourse to direct substitution, which is not always practicable.

The left hand column of the following table contains a list of those metallic or basylenous elements which unite in one proportion only with the four non-metallic or chlorous elements in the right hand column, the numbers opposite to each element showing the proportions in which the combination takes place (*e.g.*, 12 magnesium with 35.5 chlorine, 39.1 potassium with 80 bromine, etc.), or, in other words, the equivalent weights:—

| | Equiv. | | Equiv. |
|-------------------|--------|------------------|--------|
| Hydrogen | 1 | Fluorine | 19 |
| Beryllium | 4.7 | Chlorine | 35.5 |
| Aluminium | 9.13 | Bromine | 80 |
| Lithium | 7 | Iodine | 127 |
| Magnesium | 12 | | |
| Calcium | 20 | | |
| Sodium | 23 | | |
| Zinc | 32.6 | | |
| Indium | 37.7 | | |
| Potassium | 39.1 | | |
| Strontium | 43.8 | | |
| Barium | 68.7 | | |
| Rubidium | 85.4 | | |
| Cesium | 133 | | |

These numbers, as will be explained further on, are also the relative quantities of the several elements which would be separated from their compounds by an electric current of given strength: thus, if the same current were passed through solutions of sodium bromide, potassium iodide, and zinc chloride, the quantities of sodium, potassium, zinc, bromine, iodine, and chlorine simultaneously separated would be to one another in the proportion of the numbers in the table.

In most cases, however, combination between two elements takes place in more than one proportion, and in such cases the notion of equivalent value becomes less definite; in fact, such elements may be said to have as many equivalent weights as there are ways in which they can combine with others. Thus, tin forms two series of compounds, the stannous compounds, in which 59 parts of the metal unite with 35.5 of chlorine, 80 of bromine, 127 of iodine, etc., and the stannic compounds, in which half that quantity of tin, viz., 29.5 parts, discharges the same function; tin has therefore two equivalents, viz., 59 in the stannous and 29.5 in the stannic compounds. In like manner, the equivalent of iron is 28 in the ferrous and 18 $\frac{2}{3}$ in the ferric compounds.*

Atomic Weights.—Let us now compare the hydrogen compounds of chlorine, oxygen, nitrogen, and carbon with regard to the manner in which the hydrogen contained in them may be replaced by other elements. Compare first hydrochloric acid and water. When hydrochloric acid is acted upon by sodium, the whole of the hydrogen is expelled, and the chlorine enters into combination with an equivalent quantity of the metal; thus 35.5 parts hydrochloric acid (= 1 part hydrogen + 35.5 chlorine) and 23 sodium yield 1 part of free hydrogen and 23 + 35.5 (=58.5) sodium chloride; there is no such thing as the expulsion of part of the hydrogen, or the formation of a compound containing both hydrogen and metal in combination with the chlorine.

With water, however, the case is different. When sodium is thrown upon water, 18 parts of that compound (= 2 hydrogen + 16 oxygen) are decomposed, in such a manner that half of the hydrogen is expelled by

* In such cases it is sometimes supposed that the two classes of compounds contain different metallic radicles, combined with the same quantity of a non-metallic or chlorous element, the stannous compounds, for example, being supposed to contain a radicle called *stannoxum* (eq. 59), and the stannic compounds another radicle called *stannicum* (eq. 29.5). This, however, is a mere mode of expression, since, to take the two chlorides of tin for example, these two compounds might just as well be supposed to contain different chlorous radicles combined with the same quantity of tin.

an equivalent quantity of sodium, 23, and sodium hydroxide is formed, containing—

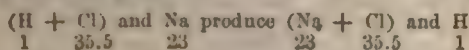
| Sodium. | Hydrogen. | Oxygen. |
|---------|-----------|---------|
| 23 | + | 1 |
| | | + |
| | | 16 |

This compound remains in the solid state when the liquid is evaporated to dryness; and if it be further heated in a tube with sodium, the remaining half of the hydrogen is driven off, and anhydrous sodium-oxide remains, composed of 46 parts sodium + 16 oxygen.

Water differs, therefore, from hydrochloric acid in this respect, that its hydrogen may be replaced by sodium in two equal portions, yielding successively a hydroxide and an anhydrous oxide, the relations of which to the original compound may be thus represented:—

| Water. | | Sodiumhydroxide. | | | Sodiumoxide. | |
|-----------|-----|------------------|------|-----|--------------|-----|
| Hydrogen. | Ox. | Hyd. | Sod. | Ox. | Sodium. | Ox. |
| (1 + 1) | + | 1 | + | 23 | (23 + 23) | + |
| | 16 | | | 16 | | 16. |

Regarding these results in connection with the atomic hypothesis of the constitution of bodies, we may suppose: (1) That each molecule of hydrochloric acid is composed of one atom of hydrogen and one atom of chlorine, and that when this compound is acted upon by sodium, each molecule is decomposed, its hydrogen-atom being driven out and replaced by an atom of sodium: thus—



The weights of the three atoms concerned in this reaction are to one another in the same proportion as the equivalent weights, or, taking the hydrogen as the unit in each case, we may say that the atomic weights of sodium and chlorine are identical with their equivalent weights.

(2) Each molecule of water must be supposed to contain two atoms of hydrogen: for if it contained only one atom, then, since the first action of the sodium is to expel only half the hydrogen, it would follow that each atom of hydrogen would be split into two, and that each molecule of sodium hydroxide would contain only half an atom of hydrogen; this, however, is at variance with the fundamental notion of atoms, namely, that they are indivisible. These two atoms of hydrogen are combined with a quantity of oxygen weighing 16, which is, therefore, the smallest quantity of oxygen capable of entering into the reaction under consideration.—



and we shall hereafter find that the same is true with regard to all other well-defined reactions in which oxygen takes part. Hence this quantity of oxygen, 16 parts by weight (hydrogen being the unit), is regarded as the weight of the atom of oxygen.

This atomic weight of oxygen is not equal to the equivalent weight, as in the case of chlorine, but *twice as great*, 8 parts of oxygen being the quantity which is capable of replacing one part of hydrogen in combination, and may in many cases be directly substituted for it, as when alcohol, a compound of 12 parts carbon, 3 hydrogen, and 8 oxygen, is oxidized to acetic acid containing 12 carbon, 2 hydrogen, and 16 oxygen.

Let us now consider the hydrogen-compound of nitrogen, that is to say, *ammonia*. This is composed of 1 part of hydrogen united with $\frac{14}{3}$ or $\frac{1}{3}$ of nitrogen. Now in this compound the hydrogen is replaceable by thirds,

or 3 parts hydrogen with 14 parts nitrogen. When potassium is heated in ammonia gas, a compound called potassamine is formed, in which one-third of the hydrogen is replaced by potassium. Another compound, called tripotassamine, is also known, consisting of ammonia in which the whole of the hydrogen is replaced by an equivalent quantity of potassium.

There is also a large class of compounds derived from ammonia in like manner by the replacement of $\frac{1}{3}$, $\frac{2}{3}$, or the whole of the hydrogen by equivalent quantities of certain groups of elements called *compound radicals* (see page 238). Hence, by reasoning similar to that which was above applied to water, it is inferred that the molecule of ammonia contains 3 atoms of hydrogen, and that the atomic weight of nitrogen is 14. Moreover, in certain organic compounds, this quantity of nitrogen may be substituted for 3 parts of hydrogen, or $\frac{1}{3}$ nitrogen for 1 hydrogen; consequently the atomic weight of nitrogen is three times its equivalent weight.

Next take the case of *marsh gas* or *methane*, a compound of 1 part hydrogen with 3 parts carbon, or 4 of hydrogen with 12 of carbon. When this gas is mixed with chlorine, and exposed to diffuse daylight, a new compound is formed, in which one-fourth of the hydrogen belonging to the marsh gas is replaced by an equivalent quantity of chlorine; and if the chlorine is in excess, and the mixture exposed to sunshine, three other compounds are formed, in which one-half, three-fourths, and all the hydrogen, are thus replaced. The results may be thus expressed:—

| | | | | | | | | |
|---------|---|---|---|------|---|------|---|-----------|
| Carbon. | | Methane.
Hydrogen. | | | | | | |
| 12 | + | 1 | + | 1 | + | 1 | + | 1 |
| Carbon. | | Chloromethane.
Hydrogen. | | | | | | Chlorine. |
| 12 | + | 1 | + | 1 | + | 1 | + | 35.5 |
| Carbon. | | Dichloromethane.
Hydrogen. | | | | | | Chlorine. |
| 12 | + | 1 | + | 1 | + | 35.5 | + | 35.5 |
| Carb. | | Trichloromethane or Chloroform.
Hyd. | | | | | | Chlorine. |
| 12 | + | 1 | + | 35.5 | + | 35.5 | + | 35.5 |
| Carbon. | | Tetrachloromethane.
Chlorine. | | | | | | |
| 12 | + | 35.5 | + | 35.5 | + | 35.5 | + | 35.5 |

Hence, by reasoning similar to the above, it is inferred that the molecule of methane contains 4 atoms of hydrogen, and that the atomic weight of carbon is 12. Moreover, as this quantity of carbon can unite with 4×35.5 parts, or 4 atoms of chlorine, it follows that the atomic weight of carbon is equal to four times its equivalent weight.

We have thus shown in three cases how the atomic weight of an element may be determined by the proportion in which equivalent substitution takes place in its compounds with hydrogen. Sulphur, selenium, and tellurium, form hydrogen-compounds exactly analogous in this respect to water, the hydrogen being replaceable by halves; their atomic weights

are, therefore, double of their equivalent weights. Silicon forms with chlorine a compound containing 7 parts silicon with 35.5 parts chlorine; and in this one-fourth of the chlorine is replaceable by hydrogen or by carbon: hence the atomic weight of silicon is, like that of carbon, equal to four times the equivalent weight, its numerical value being 28. There are also some elements in which the atomic weight is equal to five times, six in which it is equal to six times, and others in which it is perhaps equal to seven times or eight times the equivalent weight: higher ratios have not been observed.

It must not be supposed that the atomic weights of elementary bodies are always actually determined in the manner above described. There are several other methods of determining their numerical values, as will be presently explained; and the values obtained by different methods do not always exhibit exact agreement; but the atomic weights of all the more important elements may be regarded as definitely fixed within small numerical errors. The equivalent value of an element, or the ratio of the equivalent to the atomic weight, is also subject to some variation, as will be presently explained, according to the view which may be taken of the constitution of particular compounds.

The values of the atomic weights on which chemists are now, for the most part, agreed, are given in the table on page 27.

Physical and Chemical Relations of Atomic Weights.

The atomic weights of the elementary bodies exhibit some remarkable relations to their physical properties, and to the proportions in which they unite by volume.

1. To the Specific Heats of the Elementary Bodies.—Dulong and Petit, in the course of their investigations on specific heat, observed that, if the specific heats of bodies be computed upon equal weights, numbers are obtained all different, and exhibiting no simple relations amongst themselves; but if, instead of equal weights, quantities be taken in the proportion of the atomic weights, the resulting specific heats come out very nearly equal, at least in the case of solid and liquid elements, showing that some exceedingly intimate connection must exist between the relation of bodies to heat, and their chemical nature.

In the following table, the solid and liquid elementary bodies are arranged in the order of their specific heats, as determined by Regnault, beginning with those whose specific heat is the greatest; and this order, it will be observed, is the inverse of that of the atomic weights in the third column:—

Specific Heats of Elementary Bodies.

| Elements. | Specific Heat
(that of
Water = 1.) | Atomic
Weights. | Product of
Sp. Heat \times
At. Weight. |
|-------------------------------|--|--------------------|--|
| Lithium | 0.9408 | 7 | 6.59 |
| Sodium | 0.2934 | 23 | 6.75 |
| Aluminium | 0.2143 | 27.4 | 5.89 |
| Phosphorus { liquid | 0.2120 | } 31 { | 6.57 |
| { solid | 0.1887 | | 5.85 |
| Sulphur | 0.2026 | 32 | 6.48 |
| Potassium | 0.1696 | 39 | 6.61 |
| Iron | 0.1138 | 56 | 6.37 |
| Nickel | 0.1086 | 58.8 | 6.37 |
| Cobalt | 0.1070 | 58.8 | 6.28 |
| Copper | 0.0952 | 63.4 | 6.04 |
| Zinc | 0.0956 | 65.2 | 6.24 |
| Arsenic | 0.0814 | 75 | 6.10 |
| Selenium | 0.0762 | 79.4 | 6.02 |
| Bromine (solid) | 0.0843 | 80 | 6.75 |
| Palladium | 0.0593 | 106.6 | 6.31 |
| Silver | 0.0570 | 108 | 6.16 |
| Cadmium | 0.0567 | 112 | 6.35 |
| Indium | 0.0570 | 113.4 | 6.46 |
| Tin | 0.0562 | 118 | 6.63 |
| Antimony | 0.0508 | 122 | 6.19 |
| Iodine | 0.0541 | 127 | 6.87 |
| Tellurium | 0.0474 | 128 | 6.06 |
| Gold | 0.0324 | 197 | 6.38 |
| Platinum | 0.0311 | 197.4 | 6.15 |
| Mercury { solid | 0.0319 | } 200 { | 6.38 |
| { liquid | 0.0333 | | 6.66 |
| Thallium | 0.0335 | 204 | 6.83 |
| Lead | 0.0314 | 207 | 6.50 |
| Bismuth | 0.0308 | 210 | 6.48 |

A comparison of the numbers in the fourth column of this table shows that, for a considerable number of elementary bodies in the solid state, the specific heats are very nearly proportional to the atomic weights, so that the products of the specific heats of the elements into their atomic weights give nearly a constant quantity, the mean value being 6.4. This quantity may be taken to represent the *atomic heat* of the several elements in the solid state, or the quantity of heat which must be imparted to or removed from atomic proportions of the several elements, in order to produce equal variations of temperature.

Carbon, boron, and silicon were formerly regarded as exceptions to this law, their atomic heats, calculated from the specific heats determined at ordinary temperatures, being considerably below the mean value of those of the other elements, as shown by the following table:—

| Elements. | | Specific Heat. | Atomic Weights. | Product of Sp. Heat \times Atomic Weight. |
|-----------|---------------|----------------|-----------------|---|
| Boron | | 0.2500 | 11 | 2.75 |
| Carbon | wood charcoal | 0.2415 | 12 | 2.90 |
| | graphite | 0.2008 | | 2.41 |
| | diamond | 0.1469 | | 1.76 |
| Silicon | crystallized | 0.1774 | 28 | 4.97 |
| | fused | 0.1750 | | 4.70 |

F. Weber has, however, lately shown* that the specific heats of these three bodies increase rapidly at higher temperatures, and that at particular temperatures (about 6000° for carbon) they become constant, giving for the atomic heats a mean value of about 6, which is nearly the same as that of other elements of small atomic weight, like aluminium and phosphorus, thus:—

| | Sp. Heat. | At. Weight. | At. Heat. |
|---------|-----------|-------------|-----------|
| Silicon | 0.203 | 28 | 5.7 |
| Carbon | 0.467 | 12 | 5.6 |
| Boron | 0.5 | 11 | 5.5 |

The specific heats and molecular weights of similarly constituted compounds exhibit, for the most part, the same relation as that which is observed between the specific heats and atomic weights of the elements.

2. To the Crystalline Forms of Compounds.—It is found that, in many cases, two or more compounds which, from chemical considerations, are supposed to contain equal numbers of atoms of their respective elements, crystallize in the same or in very similar forms. Such compounds are said to be *isomorphous*.† Thus, the sulphates constituted like magnesium sulphate, $MgSO_4 + 7H_2O$, are isomorphous with the corresponding chlorates, $MgClO_4 + 7H_2O$.

Accordingly, these isomorphous relations are often appealed to for the purpose of fixing the constitution of compounds, and thence deducing the atomic weights of their elements, in cases which would otherwise be doubtful. Thus, aluminium forms only one oxide, viz., alumina, which is composed of 15.3 parts by weight of aluminium and 16 parts of oxygen. What, then, is the atomic weight of aluminium? The answer to this question will depend upon the constitution assigned to alumina, whether it is a monoxide, sesquioxide, dioxide, etc. Thus:—

| | | O. | AL |
|-------------|-------------|------|--------|
| Monoxide | $AlO =$ | 16 + | 18.3 |
| Sesquioxide | $Al_2O_3 =$ | 48 + | { 27.4 |
| Dioxide | $AlO_2 =$ | 32 + | { 27.4 |
| Trioxide | $AlO_3 =$ | 48 + | { 36.6 |
| | | | 54.8 |

The numbers in the last column of this table are the weights which must be assigned to the atom of aluminium, according to the several modes of constitution indicated in the first column; but there is nothing in the constitution of the oxide itself that can enable us to decide between them. Now, iron forms two oxides, in which the quantities of oxygen united with

* Ann. Chim. Phys. [5] viii. 132.

† *Isom. equal; morph. form.*

the same quantity of iron are to one another as 1 : $1\frac{1}{2}$, or as 2 : 3. These are therefore regarded as monoxide, FeO , and sesquioxide, Fe_2O_3 , and this last oxide is known to be isomorphous with alumina. Consequently, alumina is also regarded as a sesquioxide, Al_2O_3 , and the atomic weight of aluminium is inferred to be 27.4.

3. To the Volume-relations of Elements and Compounds.—The atomic weights of those elements which are known to exist in the state of gas or vapor are, with one or two exceptions, proportional to their specific gravities in the same state. Taking the specific gravity of hydrogen as unity, those of the following gases and vapors are expressed by numbers identical with their atomic weights:—

| | | | |
|--------------------|------|---------------------|-----|
| Hydrogen | 1 | Oxygen | 16 |
| Chlorine | 35.5 | Sulphur | 32 |
| Bromine | 80 | Selenium | 79 |
| Iodine | 127 | Tellurium | 128 |

The exceptions to this rule are exhibited by *phosphorus* and *arsenic*, whose vapor-densities are twice as great as their atomic weights, that of phosphorus being 62, and that of arsenic 150; and by *mercury* and *cadmium*, whose vapor-densities are the halves of their atomic weights, that of mercury being 100, and that of cadmium 56.

From these relations, considered in connection with the above explained laws of combination by weight, it follows that the volumes of any two elementary gases which make up a compound molecule, are to one another in the same ratio as the number of atoms of the same elements which enter into the compound, excepting in the case of phosphorus and arsenic, for which the number of volumes thus determined has to be halved, and of mercury and cadmium, for which it must be doubled: thus—

| The molecule | HCl | contains | 1 vol. H | and 1 vol. Cl |
|--------------|------------------------|----------|-----------|--------------------|
| " | H_2O | " | 2 " H | 1 " O |
| " | H_3N | " | 3 " H | 1 " N |
| " | H_3P | " | 3 " H | $\frac{1}{2}$ " P |
| " | | " | or 6 " H | 1 " P |
| " | Cl_3As | " | 3 " Cl | $\frac{1}{2}$ " As |
| " | | " | or 6 " Cl | 1 " As |
| " | Cl_2Hg | " | 2 " Cl | 2 " Hg |

If the smallest volume of a gaseous element that can enter into combination be called the combining volume of that element, the law of combination may be expressed as follows: *The combining volumes of all elementary gases are equal, excepting those of phosphorus and arsenic, which are only half those of the other elements in the gaseous state, and those of mercury and cadmium, which are double those of the other elements.*

It appears, then, that in all cases the volumes in which gaseous elements combine together may be expressed by very simple numbers. This is the "Law of Volumes," first observed by Humboldt and Gay-Lussac in 1805, with regard to the combination of oxygen and hydrogen, and afterwards established in other cases by Gay-Lussac, whose observations, published in his "Theory of Volumes," afforded new and independent evidence of the combination of bodies in definite and multiple proportions, in corroboration of that derived from the previously observed proportions of combination by weight.

Gay-Lussac likewise observed that the product of the union of two gases, when itself a gas, sometimes retains the original volume of its constituents, no contraction or change of volume resulting from the com-

blation, but that when contraction takes place, which is the most common case, the volume of the compound gas always bears a simple ratio to the volumes of its elements: and subsequent observation, extended over a very large number of compounds, organic as well as inorganic, has shown that, with a few exceptions, probably only apparent, *the molecules of compound bodies in the gaseous state occupy twice the volume of an atom of hydrogen gas.* No matter what may be the number of atoms or volumes that enter into the compound, they all become condensed into two volumes: thus—

| | | | | | | | | | | | |
|---|------|---|-----|---------------|------|----|------|---|------|-------------------|---------------------|
| 1 | vol. | H | and | 1 | vol. | Cl | form | 2 | vol. | HCl, | hydrochloric acid. |
| 1 | " | N | " | 1 | " | O | " | 2 | " | NO, | nitrogen dioxide. |
| 2 | " | H | " | 1 | " | O | " | 2 | " | H ₂ O, | water. |
| 3 | " | H | " | 1 | " | N | " | 2 | " | H ₂ N, | ammonia. |
| 3 | " | H | " | $\frac{1}{2}$ | " | P | " | 2 | " | H ₂ P, | hydrogen phosphide. |

Similarly in the union of compound gases, *e. g.*—

| | | | | | | | | | | | | |
|---|------|---------|---------------------------------|-----|---|------|----|------|---|------|--|------------------|
| 1 | vol. | ethyl, | C ₂ H ₅ , | and | 1 | vol. | Cl | form | 2 | vol. | C ₂ H ₅ Cl, | ethyl chloride. |
| 2 | " | ethyl, | C ₂ H ₅ , | " | 1 | " | O | " | 2 | " | (C ₂ H ₅) ₂ O, | ethyl oxide. |
| 2 | " | ethene, | C ₂ H ₄ , | " | 2 | " | Cl | " | 2 | " | C ₂ H ₄ Cl ₂ , | ethene chloride. |
| 2 | " | ethene, | C ₂ H ₄ , | " | 1 | " | O | " | 2 | " | C ₂ H ₄ O, | ethene oxide. |

It will presently be shown, as at least highly probable, that the molecule of an elementary gas in the free state is made up of two atoms, H₂, for example. The law just enunciated may, therefore, be generalized as follows: *The molecules of all gases, simple or compound, occupy equal volumes; or, equal volumes of all gases contain equal numbers of molecules.*

This is called the "Law of Avogadro," having been first enunciated (in 1811) by an Italian physicist of that name. It is quite in accordance with the observed fact that all perfect gases, simple and compound, are equally affected by equal variations of pressure and temperature; and indeed it may be shown, by mathematical reasoning, to follow as a necessary consequence from the physical constitution of gases as explained in connection with the dynamical theory of heat (pp. 76-81): but the demonstration is not of a nature adapted for an elementary book. The law may, however, be considered as completely established by the relations between the combining proportions of the elements by weight and by volume as already explained, and it is now regarded as affording the surest method of fixing the molecular constitution of all compounds that can be obtained in the gaseous state, and the atomic weights of the elements contained in them.

Suppose, for example, it were required to determine the atomic weight of tin. This metal forms a volatile chloride (stannic chloride), in which 29.5 parts by weight of tin are combined with 35.5 parts of chlorine: 29.5 is, therefore, the equivalent of tin in this compound. Now the vapor-density of this chloride, or the weight of one volume referred to hydrogen as unity, is 135; consequently the weight of two volumes of the vapor is 270, and this contains 118 parts of tin and 4×35.5 or 142 of chlorine; and as this appears to be the chloride containing the largest proportion of chlorine, or the smallest proportion of tin, it is regarded as a compound of 4 atoms of chlorine and 1 atom of tin, and the atomic weight of tin is thus found to be 118.

When an element does not form any volatile compounds whose vapor-densities can be exactly ascertained, its atomic weight may be determined by its specific heat, according to the law of Dulong and Petit (p. 221), or by its isomorphous relations with other elements, as already explained in the case of aluminium. To give an instance of the determination of the

atomic weight of an element according to its specific heat, we may take the case of indium. This metal forms a chloride containing 35.5 parts of chlorine and 37.8 parts of indium, which latter number is, therefore, the equivalent weight of the metal. Now when indium was first discovered (in 1863), this chloride was, for reasons which need not here be specified, regarded as a dichloride, InCl_2 , and consequently the atomic weight of indium was supposed to be 75.6. Subsequently, however, Bunsen showed that the specific heat of indium, referred to the unit of weight, is 0.057, and this number multiplied by 75.6 gives for the atomic heat the number 4.5, which does not agree with the law of Dulong and Petit; but if the chloride be regarded as a trichloride, MCl_3 , making the atomic weight of the metal equal to three times its equivalent weight, or 113.4, the atomic heat becomes 6.15, which agrees very nearly with the general law. This number 113.4 is, therefore, now adopted as the atomic weight of indium.

Specific or Atomic Volume.

These terms denote the quotient obtained by dividing the molecular weight of a body by its specific gravity. Now, from the law of condensation in the combination of gases above detailed (p. 228), it follows that *the specific gravity of any compound gas or vapor, referred to hydrogen as unity, is equal to half its atomic or molecular weight*: hence also, *the specific volumes of compound gases or vapors, referred to that of hydrogen as unity are, with a few exceptions, equal to 2*. It will presently be shown that the same law applies to the specific volumes of the elementary gases themselves.

Some compounds, however, exhibit a departure from this rule, their observed specific gravities being equal to only one-fourth their molecular weights, or their molecules occupying four times the volume of an atom of hydrogen. Such is the case with sal-ammoniac, NH_4Cl , phosphorus pentachloride, PCl_5 , sulphuric acid, H_2SO_4 , ammonium hydresulphide (NH_4SH), and a few others. This anomaly is probably due, in some at least, to a decomposition or "dissociation" of the compound at the high temperature to which it is subjected for the determination of its vapor-density: NH_4Cl , for example, splitting up into NH_3 and HCl , each of which occupies two volumes, and the whole therefore four volumes; and in like manner H_2SO_4 may be supposed to separate into H_2O and SO_3 ; PCl_5 into PCl_3 and Cl_2 ; (NH_4SH into NH_3 and H_2S , etc.

On the other hand, some substances, both simple and compound, exhibit, at temperatures not far above their boiling points, vapor-densities considerably greater than they should have according to the general law, whereas when raised to higher temperatures they exhibit normal vapor-densities. Thus sulphur, which boils at 440° , exhibits at 1000° , like elementary gases in general, a vapor-density equal to its atomic weight, viz., 32; but at 500° its vapor-density is nearly three times as great. Again, acetic acid, $\text{C}_2\text{H}_4\text{O}_2$, whose molecular weight is $24 + 4 + 16 = 60$, has, at temperatures considerably above its boiling point, a vapor-density nearly equal to 30; but at 125° (8 degrees above its boiling point), its vapor-density is rather more than 45, or $1\frac{1}{2}$ times as great. This anomalous increase of vapor-density appears to take place when the substance approaches its liquefying point, at which also it exhibits irregularities in its rate of expansion and contraction by variations of pressure and temperature—at which, in short, it begins to behave itself like a liquid: but at higher temperatures it exhibits the physical characters of a perfect gas, and then also its specific gravity becomes normal.

Specific Volumes of Liquids and Solids.—The following table exhibits the specific volumes of those solid and liquid elements whose specific gravities have been determined with sufficient accuracy. The elements are arranged in the order of their specific volumes, beginning with the smallest:—

Specific Volumes of Solid and Liquid Elements.

| | Atomic weight | Spec. gr. | Specific volume. | | Atomic weight | Spec. gr. | Specific volume. |
|---------------------------|---------------|-----------|------------------|---------------------------|---------------|-----------|------------------|
| Carbon, as diamond . . . | 12 | 3.52 | 3.4 | Mercury, liquid . . . | 200 | 14.8 | 14.8 |
| Beryllium . . . | 9.4 | 2.1 | 4.4 | Sulphur, trimetric . . . | 32 | 2.07 | 15.2 |
| Carbon, as graphite . . . | 12 | 2.3 | 5.2 | Indium . . . | 113.4 | 7.4 | 15.3 |
| Nickel . . . | 58.8 | 8.6 | 6.8 | Phosphorus, red . . . | 31 | 1.94 | 15.8 |
| Manganese . . . | 55 | 8.03 | 6.83 | Sulphur, monoclinic . . . | 32 | 1.98 | 16.2 |
| Cobalt . . . | 58.8 | 8.30 | 7.0 | Tin . . . | 118 | 7.3 | 16.2 |
| Iron . . . | 56 | 7.8 | 7.2 | Selenium, granular . . . | 79.4 | 4.80 | 16.4 |
| Copper . . . | 63.4 | 8.95 | 7.2 | Phosphorus, yellow . . . | 31 | 1.84 | 16.8 |
| Chromium . . . | 52.2 | 7.01 | 7.4 | Antimony . . . | 122 | 6.7 | 18.2 |
| Iodine . . . | 127 | 21.8 | 9.1 | Lead . . . | 207 | 11.33 | 18.3 |
| Platinum . . . | 197.4 | 21.5 | 9.2 | Selenium, amorphous . . . | 79.4 | 4.28 | 18.4 |
| Zinc . . . | 65.2 | 7.1 | 9.2 | Tellurium . . . | 128 | 6.2 | 20.6 |
| Palladium . . . | 106.6 | 11.8 | 9.2 | Bismuth . . . | 210 | 9.8 | 21.2 |
| Rhodium . . . | 104.4 | 11.0 | 9.4 | Sodium . . . | 23 | 0.97 | 23.7 |
| Silver . . . | 108 | 10.5 | 10.2 | Calcium . . . | 40 | 1.58 | 25 |
| Gold . . . | 199 | 19.34 | 10.2 | Iodine . . . | 127 | 4.95 | 25.7 |
| Aluminium . . . | 27.4 | 2.67 | 10.26 | Bromine, liquid . . . | 80 | 3.19 | 25.8 |
| Molybdenum . . . | 96 | 8.3 | 11.1 | Chlorine, liquid . . . | 35.5 | 1.33 | 26.7 |
| Silicon, granular . . . | 28 | 2.5 | 11.2 | Strontium . . . | 87.6 | 2.54 | 34.4 |
| Barium . . . | 7 | 0.59 | 11.9 | Potassium . . . | 39.1 | 0.86 | 45.6 |
| Caesium . . . | 112 | 8.7 | 13.0 | | | | |
| Uranium . . . | 240 | 18.4 | 13.2 | | | | |
| Arsenic . . . | 75 | 5.63 | 13.3 | | | | |
| Magnesium . . . | 24 | 1.74 | 13.8 | | | | |

The numbers in the third column of this table do not exhibit the simplicity of relation which exists between the specific volumes of gaseous bodies. There are, indeed, several causes which interfere with the existence, or at least with the observation, of such simple relations between the specific volumes of solid and liquid elements. In the first place, the densities of three of them, mercury, bromine, and chlorine, are such as to belong to them in the liquid state, whereas the densities assigned to all the others have been determined in the solid state. In solids, moreover, the density is greatly affected by the state of aggregation, whether crystalline or amorphous, and in dimorphous bodies, each form has a density peculiar to itself. Further, as solids and liquids are variously affected by heat, each having a peculiar rate of expansion, and that rate being different at different temperatures, it is not to be expected that their specific volumes should exhibit simple relations, unless they are compared at temperatures at which they are similarly affected by heat. Even gases are found to exhibit abnormal specific volumes if compared at temperatures too near the points at which they pass into the liquid state. In liquids, the simplest relations of specific volume are found at those temperatures for which the tensions of the vapors are equal (Kopp); and in solids, the melting points are most probably the comparable temperatures. Now the

specific gravities of most of the solid elements in the preceding table have been determined at mean temperatures (as at 15.5° C., 60° F.), which, in the case of potassium, sodium, phosphorus, and a few others, do not differ greatly from the melting points, but in other cases, as with gold, platinum, iron, etc., are removed from the melting points by very long intervals. In spite, however, of these causes of divergence, the specific volumes of certain analogous elements are very nearly equal to each other: viz., those of selenium and sulphur; of chromium, iron, cobalt, copper, manganese, and nickel; of molybdenum and tungsten; of iridium, platinum, palladium, and rhodium; and of gold and silver.

Specific Volumes of Solid and Liquid Compounds.—The most general relation that has been observed between the specific volumes of solid compounds is, that *isomorphous compounds have equal specific volumes*, in other words, that their densities are proportional to their molecular weights: such is the case, for example, with the native carbonates of strontium (strontianite) and of lead (cerussite):

| Formula. | Molecular weight. | Specific gravity. | Specific volume. |
|-----------------|-------------------|-------------------|------------------|
| SrCO_3 | 147.6 | 3.60 | 41.0 |
| PbCO_3 | 267 | 6.47 | 41.3 |

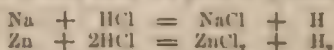
If the crystalline forms are only approximately similar, the specific volumes also are only approximately equal, the difference being less as the angles of the two crystalline forms are more nearly equal and their axis more nearly in the same ratio. In dimorphous compounds, each modification has a density, and therefore a specific volume, peculiar to itself.

The hydrated sulphates of magnesium, zinc, nickel, cobalt, and iron, which have the general formula, $\text{M''SO}_4 + 7\text{H}_2\text{O}$ (M'' denoting a bivalent metal: see next page), and crystallize in similar forms, have specific volumes very nearly equal to 146; the double sulphates isomorphous with potassio-cupric sulphate, $\text{K}_2\text{Cu}(\text{SO}_4)_2 + 6\text{H}_2\text{O}$, have specific volumes ranging between 198 and 216; and the alums, e. g., $\text{KAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$, have specific volumes ranging between 276 and 281.

The specific volumes of liquid compounds have been studied chiefly with relation to organic compounds. The most general relation observed is that: *Differences of specific volumes are in numerous instances proportional to the differences between the corresponding chemical formulae.* Thus liquids whose formulae differ by $n\text{CH}_2$ differ in specific volume by n times 22; for example, methyl formate CH_3CHO , and ethyl butyrate $\text{C}_2\text{H}_5\text{C}_4\text{H}_7\text{O}_2$, which differ by 4CH_2 , have specific volumes differing by nearly 4×22 .

Atomicity, Quantivalence.

We have seen that the atomic weight of an element is in some cases equal to its equivalent weight, in others, twice, three times, four times, etc., as great as the equivalent weight; in other words, an atom of certain elements can replace or be substituted for only one atom of hydrogen, whereas the atoms of other elements can replace 1, 2, 3, 4, etc., atoms of hydrogen. Thus, when sodium dissolves in hydrochloric acid, each atom of sodium replaces 1 atom of hydrogen; but when zinc dissolves in the same acid, each atom of zinc takes the place of 2 atoms of hydrogen: thus



Here it is seen that an atom of zinc is equal in combining, or saturating power to 2 atoms of hydrogen. In like manner, antimony and bismuth form trichlorides, AlCl_3 and BiCl_3 , in which the atom of the metal per-

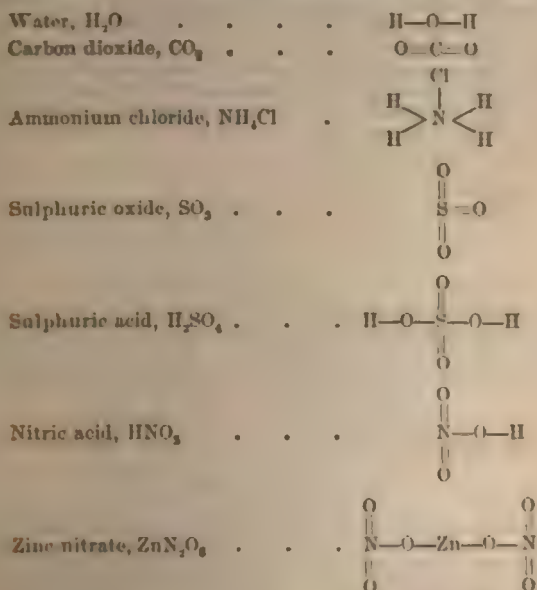
forms the same chemical function as 3 atoms of hydrogen, that is to say, it saturates 3 atoms of chlorine; so also tin in the tetrachloride is equivalent to 4H, and phosphorus in the pentachloride, PCl_5 , to 5H.

This difference of equivalent, combining, or saturating power is called *valence* or *atomicity*, and is sometimes denoted by placing *dots* or *Roman numerals* to the right of the symbol of an element, and at the top, as O'' , B''' , C^v , etc.; and the several elements are designated

| | |
|--|--|
| Univalent elements, or Monads, as H | |
| Bivalent " Dyads, " O'' | |
| Trivalent " Triads, " B''' | |
| Quadrivalent " Tetrads, " C^v | |
| Quinivalent " Pentads, " P^v | |
| Sextivalent " Hexads, " W^v | |

Elements of even equivalency, viz., the dyads, tetrads, and hexads, are also included under the general term *artiads*,* and those of uneven equivalency, viz., the monads, triads, and pentads, are designated generally as *perissads*.†

Another method of indicating the equivalent values of the elementary atoms, and the manner in which they are satisfied by combination, is to arrange the symbols in diagrams in which each element is connected with others by a number of lines, or connecting bonds corresponding with its degree of equivalency; a monad being connected with other elements by only one such bond, a triad by three, a hexad by six, etc., as in the following examples:—



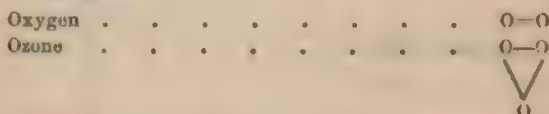
* *Artios*, even.

† *Perissos*, uneven.

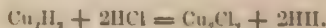
It must be distinctly understood that these formulæ—which are called graphic, structural, or constitutional formulæ—are not intended to represent the actual arrangement of the atoms in a compound; indeed, even if we had a distinct notion of the manner in which the atoms of any compound are arranged, it could not be adequately represented on a plane surface. The lines connecting the different atoms indicate nothing more than the number of units of equivalency belonging to the several atoms, and the manner in which they are disposed of by combination with those of other atoms. Thus, the formula for nitric acid indicates that two of the three constituent oxygen atoms are combined with the nitrogen alone, and are consequently attached to that element by both their units of equivalency, whereas the third oxygen atom is combined both with nitrogen and with hydrogen.*

By inspection of the preceding diagrams, it will be observed that every atom of a compound has each of its units of equivalency satisfied by combination with a unit belonging to some other atom. Such, indeed, is the case in every saturated or normal compound. Accordingly, it is found that in all such compounds the sum of the perissad elements is always an even number. Thus, a compound may contain two, four, six, etc., monad atoms, as CH_4 , OH_2 , CH_2 , C_2H_6 , C_3H_8 , SiH_2Cl ; or one monad and one triad atom, as BCl_3 ; or one pentad and five monads, as NH_4Cl ; but never an uneven number of perissad atoms. This is the "law of even numbers," announced some years ago by Gerhardt and Laurent as a result of observation. It was long received with doubt, but has now been confirmed by the analysis of so many well-defined compounds, that a departure from it is looked upon as a sure indication of incorrect analysis.

For a similar reason, the atoms of elementary bodies rarely exist in the free state, but, when separated from any compound, tend to combine with other atoms, either of the same or of some other element. Perissad elements, like hydrogen, chlorine, nitrogen, etc., separate from their compounds in pairs; their molecule contains two atoms, *e. g.*, $\text{H}-\text{H}$. Artiad elements may unite in groups of two, three, or more; thus, the molecule of oxygen, in its ordinary state, probably contains two atoms, that of ozone three atoms; thus—



The tendency of elementary atoms to separate in groups is shown in various ways. Thus, when copper hydride, Cu_2H_2 (to be hereafter described), is decomposed by hydrochloric acid, a quantity of hydrogen is given off equal to twice that which is contained in the hydride itself; thus—

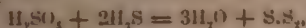


This action is precisely analogous to that of hydrochloric acid on cuprous oxide:

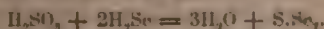


* For lecture and class illustration, solid diagrams are constructed, with wooden balls of various colors, to represent the atoms, having holes for the insertion of connecting rods; these representations are called *glyptic formulæ*. Objection is sometimes made to the use of such illustrations, on the ground that they might lead the pupils to imagine that the atoms forming a molecule are actually connected together by material bonds. As well might objection be taken to the use of an artificial globe in teaching geography and astronomy, lest the student should acquire curious notions about the brazen meridian and wooden horizon.

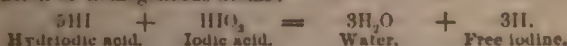
In the latter case, the hydrogen separated from the hydrochloric acid unites with oxygen, in the former with hydrogen. Again, when solutions of sulphurous acid and sulphydric acid are mixed, the whole of the sulphur is precipitated :



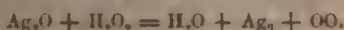
the action being similar to that of sulphurous acid on selenhydric acid :—



In the one case, a sulphide of selenium is precipitated ; in the other a sulphide of sulphur. The precipitation of iodine, which takes place on mixing hydriodic acid with iodic acid, affords a similar instance of the combination of homogeneous atoms :



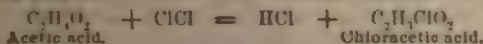
Another striking illustration of this mode of action is afforded by the reduction of certain metallic oxides by hydrogen dioxide. When silver oxide is thrown into this liquid, water is formed, the silver is reduced to the metallic state, and a quantity of oxygen is evolved equal to twice that which is contained in the silver oxide :—



Further, elementary bodies frequently act upon others as if their atoms were associated in binary groups. Thus chlorine acting upon potassium oxide forms two compounds, the chloride and hypochlorite of potassium —(p. 181) :



Again, in the action of chlorine upon many organic compounds, one atom of chlorine removes one atom of hydrogen as hydrochloric acid, while another atom of chlorine takes the place of the hydrogen thus removed. For example, in the formation of chloroacetic acid by the action of chlorine on acetic acid :—



Similarly, when metallic sulphides oxidize in the air, both the metal and the sulphur combine with oxygen ; and sulphur acting upon potash forms both a sulphide and a thiosulphate. In all these cases the atoms of the elementary bodies act in pairs.

On the supposition that the molecules of elementary bodies in the gaseous state are made up of two atoms, the specific volumes of these gases will come under the same law as that which applies to compounds (p. 230) : and it may then be stated generally, that, with the few exceptions already noticed, the specific gravities of all bodies, simple and compound, in the gaseous state, are equal to half their molecular weights ; or the specific volumes (the quotients of the molecular weights by the specific gravities) are equal to 2.

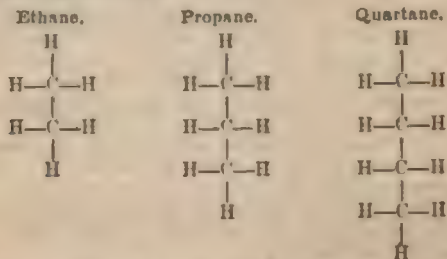
There are, however, two elements, namely, phosphorus and arsenic, which at all temperatures hitherto attained exhibit a vapor-density twice as great as that which they should have according to the general law, that of phosphorus being always 62, and that of arsenic 150. This has been explained by supposing that the molecule of each of these two elements in the free state contains four atoms instead of two, as is the case with most elementary bodies ; thus the molecule of phosphorus is supposed to be represented by the formula,



Variation of Equivalency.—Multivalent elements often exhibit varying degrees of equivalency. Thus carbon, which is quadrivalent in marsh gas, CH_4 , and in carbon dioxide, CO_2 , is only bivalent in carbon monoxide, CO ; nitrogen, which is quinquivalent in sal-ammoniac, NH_4Cl , and the other ammonium salts, and in nitrogen pentoxide, N_2O_5 , is trivalent in ammonia, NH_3 , and in nitrogen trioxide, N_2O_3 , and univalent in nitrogen monoxide N_2O ; sulphur, also, which is sexvalent in sulphur trioxide, SO_3 , is quadrivalent in sulphur dioxide, SO_2 , and bivalent in hydrogen sulphide, H_2S , and in many metallic sulphides. In these cases, and in others of varying equivalency, the variation mostly takes place by two units of equivalency. It is not very easy to account for these variations; but it is observed in all cases that the compounds in which the equivalency of a polygenic element is most completely satisfied are more stable than the others, and that the latter tend to pass into the former by taking up the required number of univalent or bivalent atoms; thus, carbon monoxide, CO , easily takes up another atom of oxygen to form the dioxide, CO_2 ; nitrogen trioxide, N_2O_3 , is readily converted into the pentoxide, N_2O_5 ; ammonia, NH_3 , unites readily with hydrochloric acid to form sal-ammoniac, NH_4Cl , etc. Similar phenomena are exhibited by many organo-metallic bodies, as will be explained further on.

From this it seems most probable that the true quantivalence or atomicity of a polygenic element is that which corresponds with the maximum number of monad atoms with which it can combine, but that one or two pairs of its units of equivalency may, under certain circumstances, remain unsaturated. Whether a saturated or an unsaturated compound is formed, will depend on a variety of conditions, often in great measure on the relative quantities of the acting substances. Thus phosphorus, which is a pentad element, forms with chlorine either a trichloride, PCl_3 , or a pentachloride, PCl_5 , according as the phosphorus or the chlorine is in excess (p. 219).*

In compounds containing two or more atoms of the same multivalent element, one or more units of equivalence belonging to each of these atoms may be neutralized by combination with those of another atom of the same kind, so that the element in question will appear to enter into the compound with less than its normal degree of equivalence. Thus in ethane, or dimethyl, C_2H_6 , which is a perfectly stable compound, having no tendency to take up an additional number of atoms of hydrogen or any other element, the carbon appears to be trivalent instead of quadrivalent; similarly in propane, C_3H_8 , its equivalence appears to be reduced to $\frac{3}{2}$; and in quartane or diethyl, C_4H_{10} , to $\frac{3}{2}$. In all these cases, however, the diminution of equivalent value in the carbon atoms is only apparent, as may be seen in the following formulae:—



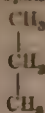
or, more shortly, omitting the equivalent marks of the monad atoms:—

* See also Erlenmeyer, *Lehrbuch der organischen Chemie*, p. 41.

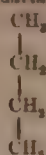
Ethane.



Propane.



Quartane.



In each of these compounds, every carbon atom, except the two outside ones, has two of its units of equivalence satisfied by combination with those of the neighboring carbon atoms, while each of the two exterior ones has only one unit thus satisfied. Hence, in any similarly constituted compound containing n carbon atoms, the number of units of equivalence remaining to be satisfied by the hydrogen atom is $4n - 2(n - 2) - 2 = 2n + 2$. The general formula of this series of hydrocarbons is, therefore, $\text{C}_n\text{H}_{2n+2}$, and the equivalent value of the carbon is $\frac{2n+2}{n}$.

In other cases, multivalent atoms may be united by two or more of their units of equivalence, so that their combining power may appear to be still further reduced, as in the hydrocarbon, C_2H_2 , in which the carbon may be apparently bivalent, and in C_2H_4 , in which it may appear to be univalent, thus—



In most cases, the equivalent value or atomicity of an element is most safely determined by the number of monad atoms with which it can combine. Of dyad atoms, indeed, any element or compound may take up an indefinite number, without alteration of its quantivalence or combining power: for each dyad atom, possessing two units of equivalence, neutralizes one unit in the compound which it enters, and introduces another, leaving, therefore, the combining power of the compound just what it was before. Thus potassium forms only one chloride, KCl , and is therefore univalent or monadic; but in addition to the oxide, K_2O , corresponding with this chloride, it likewise forms two others, viz., K_2O_2 and K_2O_4 , in the former of which it might be regarded as dyadic, and in the latter as tetradic; but the manner in which dyad oxygen enters these compounds is easily seen by inspection of the following diagrams:—

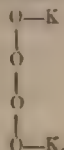
Monoxide.



Dioxide.



Tetroxide.



It is evident that any number of oxygen-atoms might, in like manner, be inserted without disturbing the balance of equivalence. If, indeed, we turn to the sulphides of potassium, in which the sulphur is dyadic, like oxygen, we find the series, K_2S , K_2S_2 , K_2S_3 , K_2S_4 , K_2S_5 , the constitution of which may be represented in a precisely similar manner. Hence the quantivalence of any element is, for the most part, best determined by the composition of its chlorides, bromides, iodides, or fluorides, rather than by that of its oxides or sulphides. In some cases, however, as will

be seen further on, the combinations of an element with oxygen afford the best means of determining its quantivalence or combining capacity.

Compound Radicles.—Suppose one or more of the component atoms of a fully saturated molecule to be removed: it is clear that the remaining atom or group of atoms will no longer be saturated, but will have a combining power corresponding with the number of units of equivalency removed. Such unsaturated groups are called residues or radicles. Methane, CH_4 , is a fully saturated compound; but if one of its hydrogen atoms be removed, the residue CH_3 (called methyl) will be ready to combine with one atom of a univalent element, such as chlorine, bromine, etc., forming the compounds CH_3Cl , CH_3Br , etc.; two atoms of it unite in like manner with one atom of oxygen, sulphur, and other bivalent elements, forming the compounds $\text{O}''(\text{CH}_3)_2$, $\text{S}''(\text{CH}_3)_2$, etc.; three atoms with nitrogen, yielding $\text{N}'''(\text{CH}_3)_3$, etc.

The removal of two hydrogen-atoms from CH_4 leaves the bivalent radicle CH_2 , called methene, which yields the compounds CH_2Cl_2 , CH_2O , CH_2S , etc. The removal of three hydrogen-atoms from CH_4 leaves the trivalent radicle CH , which, in combination with three chlorine-atoms, constitutes chloroform, CHCl_3 . And, finally, the removal of all four hydrogen-atoms from CH_4 leaves the quadrivalent radicle carbon, C^{iv} , capable of forming the compounds CCl_4 , CS_2 , etc.

In like manner, ammonia, NH_3 , in which the nitrogen is trivalent, yields, by removal of one hydrogen-atom, the univalent radicle amidogen, NH_2 , which with one atom of potassium forms potassamine, NH_2K , and when combined with one atom of the univalent radicle methyl, CH_3 , forms methylamine, $\text{NH}_2(\text{CH}_3)$, etc. The abstraction of two hydrogen-atoms from the molecule NH_3 , leaves the bivalent radicle imidogen, NH , which with two methyl-atoms forms dimethylamine, $\text{NH}(\text{CH}_3)_2$, etc.; and the removal of all three hydrogen-atoms from NH_3 , leaves nitrogen itself, which frequently acts as a trivalent element or radicle, forming tripotassamine, NK_3 , trimethylamine, $\text{N}(\text{CH}_3)_3$, etc.

Finally, the molecule of water, OH_2 , by losing an atom of hydrogen, is converted into the univalent radicle hydroxyl, OH , which, in its relations to other bodies, is analogous to chlorine, bromine, and iodine, and may be substituted in combination for one atom of hydrogen or other monads. Thus, water itself may be regarded as H.OH , analogous to hydrochloric acid, HCl ; potassium hydroxide as K.OH , analogous to potassium chloride; barium hydroxide as $\text{Ba}''(\text{OH})_2$, analogous to barium chloride, $\text{Ba}''\text{Cl}_2$.

In a similar manner, the univalent radicle, potassoxyl, KO , may be derived from potassium hydroxide; the bivalent radicle, zincoxyl, ZnO_2 , by abstraction of H_2 from zinc hydroxide, $\text{Zn}''\text{H}_2\text{O}_2$. The essential character of these oxygenated radicles is that each of the oxygen-atoms contained in them is united to the other atoms by one unit of equivalency only, so that the radicle has necessarily one or two units unconnected; thus—



From the preceding explanations of the mode of derivation of compound radicles, it is clear that there is no limit to the number of them which may be supposed to exist; in fact, it is only necessary to suppose a number of units of equivalency abstracted from any saturated molecule, in order to obtain a radicle of corresponding combining power or equivalent value. But unless a radicle can be supposed to enter into a considerable

The elements in the second row are all dyads, with the exception, perhaps, of beryllium, which has some analogies to the triads.

Of the elements in the third row, boron, gallium, indium, and thallium are undoubtedly triads. Aluminium forms a trichloride, AlCl_3 , and a corresponding oxide, Al_2O_3 , also a volatile methyl-compound, $\text{Al}(\text{CH}_3)_3$, the vapor-density of which indicates that the molecule, as represented by this formula, has the normal 2-volume condensation (p. 230). It is true that the chloride, which is also volatile, exhibits a vapor-density agreeing rather with the doubled formula, Al_2Cl_6 , which would indicate that alu-

minium is a tetrad, the chloride having the constitution $\begin{array}{c} \text{AlCl}_3 \\ | \\ \text{AlCl}_3 \end{array}$; but this

chloride boils at a very high temperature, and it is therefore probable that the temperature at which its vapor-density was actually taken was not sufficiently raised above the boiling point to bring the compound into the state of a perfect gas (p. 230).

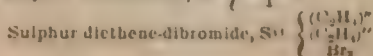
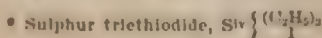
Yttrium, didymium, and erbium are usually regarded as dyads; indeed their atomic weights, as determined by experiment, are not those given in the preceding table. Mendeleeff, however, from certain considerations which will be noticed hereafter, proposes to regard them as triads, and to alter their atomic weights accordingly. The matter is, for the present, altogether doubtful, though perhaps, on the whole, the balance of argument is against Mendeleeff's suggestion.

The elements in the fourth row are undoubtedly tetrads, with the exception of lanthanum, which is more generally regarded as a dyad.

Of the elements in the fifth row, phosphorus, antimony, niobium, and tantalum form pentachlorides. Nitrogen is quivalent in the ammonium compounds, as in the chloride NH_4Cl . Vanadium, arsenic, and bismuth do not combine with more than 3 atoms of chlorine, bromine, or iodine; but bismuth forms an oxychloride, BiOCl , or $\text{O}=\text{BiCl}_2$, in which it is quivalent, and vanadium forms the analogous compound, VOCl_2 . Arsenic does not form a similar oxychloride; but its highest oxide, As_2O_5 , is the exact analogue of phosphoric oxide, P_2O_5 , and vanadic oxide, V_2O_5 , and forms a series of salts, the arsenates, which are isomorphous with the phosphates and vanadates. For these reasons, arsenic is likewise regarded as a pentad.

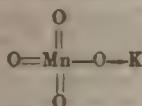
Among the elements in the sixth row, chromium forms a hexfluoride and tungsten a hexchloride; uranium forms an oxychloride, UO_2Cl_2 , and a trioxide, UO_3 . Sulphur, selenium, and tellurium, so far as regards their hydrogen compounds, H_2S , etc., are dyads; but, with regard to their combinations with chlorine, they are tetrads, and sulphur is known to form certain organic compounds in which it is tetradic, and others in which it is hexadic.* Moreover, the chemical relations of the sulphates are much more clearly represented by formulæ in which sulphur is supposed to be hexadic, like that given for sulphuric acid on p. 233, than by formulæ into which it enters as a dyad, such as $\text{H}-\text{O}-\text{O}-\text{S}-\text{O}-\text{O}-\text{H}$, inasmuch as compounds in which dyadic elements are linked together in one row, are, for the most part, very unstable, like the higher oxides and sulphides of potassium (p. 237). These three elements are therefore best regarded as hexads, though they sometimes enter into combination as tetrads, and very frequently as dyads.

Oxygen, in its combinations with hydrogen, and with most of the metals,

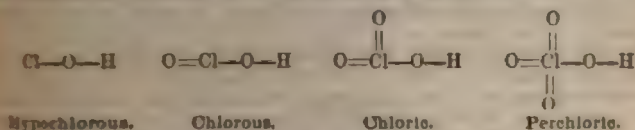


adulterately acts as a dyad; but it appears also to be capable of higher series of combination: with silver, for example, it forms the two oxides, Ag_2O and Ag_2O_2 , in the latter of which it is tetradic; and, from its close analogy to sulphur, and the place of its atomic weight in the series, it may be classed with the hexads.

Of the elements in the seventh row, manganese appears to form a heptachloride, MnCl_7 , though the composition of this chloride has not perhaps been very distinctly made out; but in the permanganates the metal appears to be decidedly heptadic; the potassium salt, KMnO_4 , for example, may be represented by the structural formula:



The perchlorates, *e. g.*, KClO_4 , are similar to the permanganates in composition and in crystalline form, and may therefore be supposed to have a similar constitution, the chlorine in them being septivalent; in fact, the hexavalent acids of chlorine form a regular series in which the quantivalence of the chlorine varies by two unites from 1 to 7; thus—



Iodic acid, IO_3H , and periodic acid, IO_4H , are exactly similar in constitution to chloric and perchloric acids, and the corresponding oxides or anhydrides I_2O_5 , I_2O_7 , are likewise known (p. 187): hence, iodine also may be regarded as a heptad. Bromic acid, BrO_3H , is similar to chloric acid, but perbromic acid has not yet been obtained; and of fluorine no oxygen-compound is known; but from the close analogy in the reactions of these elements, Cl, Br, I, and F, and the manner in which they replace one another in combination, there can be no doubt that they belong to the same group. In their combinations with hydrogen, and in the reactions in which they replace hydrogen and one another in combination, they invariably act as monads, the substitution taking place atom for atom.

Lastly, with regard to the elements (all metallic) which cannot be included in either of the seven horizontal series above considered. The atomic weights of three of these metals, *viz.*, iron, cobalt, and nickel, have values between those of manganese and copper; and of the other six, *viz.*, ruthenium, rhodium, and palladium, have atomic weights intermediate between those of molybdenum (96) and silver (108); and the other three, *viz.*, osmium, iridium, and platinum, are in like manner intermediate between tungsten (184) and gold (197).

These intermediate elements, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, constitute a group of themselves (the eighth), some of the members of which, *viz.*, Ru and Os, form tetroxides (analogous to octochlorides), and may therefore be regarded as octads. None of them, however, form chlorides containing more than 4 atoms of chlorine to one atom of metal.

The blank spaces in the preceding table indicate the places of elements which probably exist, but have not yet been actually discovered. An anticipated discovery of this kind has, however, been actually realized.

When the table was drawn up, a blank in the place now occupied by gallium indicated the probable existence of a trivalent element intermediate in atomic weight between zinc and arsenic. This element was provisionally designated *ekaluminium* by Mendelejeff, who predicted, from its position in the series, what its chief properties ought to be. The discovery of gallium, with the atomic weight 68, has verified this prediction.

CRYSTALLIZATION ; CRYSTALLINE FORM.

Almost every substance, simple or compound, capable of existing in the solid state, assumes, under favorable circumstances, a distinct geometrical figure, usually bounded by plane surfaces, and having angles of constant value. The faculty of crystallization seems to be denied only to a few bodies, chiefly highly complex organic principles, which stand, as it were, upon the very verge of organization, and which, when in the solid state, are frequently characterized by a kind of beady or globular appearance, well known to microscopical observers.

The most beautiful examples of crystallization are to be found among natural minerals, the results of exceedingly slow changes constantly occurring within the earth. It is invariably found that artificial crystals of salts, and other soluble substances which have been slowly and quietly deposited, surpass in size and regularity those of more rapid formation.

Solution in water or some other liquid is a very frequent method of effecting crystallization. If the substance be more soluble at a high than at a low temperature, then a hot and saturated solution left to cool slowly will generally be found to furnish crystals: this is a very common case with salts and various organic principles. If it be equally soluble, or nearly so, at all temperatures, then slow spontaneous evaporation in the air, or over a surface of oil of vitriol, often proves very effective.

Fusion and slow cooling may be employed in many cases: that of sulphur is a good example: the metals, when thus treated, usually afford traces of crystalline figure, which sometimes become very beautiful and distinct, as with bismuth. A third condition under which crystals very often form is in passing from the gaseous to the solid state, of which iodine affords a good instance. When by any of these means time is allowed for the symmetrical arrangement of the particles of matter at the moment of solidification, crystals are produced.

That crystals owe their figure to a certain regularity of internal structure is shown both by their mode of formation and also by the peculiarities attending their fracture. A crystal placed in a slowly evaporating saturated solution of the same substance, grows or increases by a continued deposition of fresh matter upon its sides, in such a manner that the angles formed by the meeting of the latter remain unaltered.

The tendency of most crystals to split in particular directions, called by mineralogists *cleavage*, is a certain indication of regular structure, while the optical properties of many among them, and their mode of expansion by heat, point to the same conclusion.

It may be laid down as a general rule that every substance has its own crystalline form, by which it may very frequently be recognized at once—not that each substance has a different figure, although very great diversity in this respect is to be found. Some forms are much more common than others, as the cube and six-sided prism, which are very frequently assumed by a number of bodies not in any way related.

The same substance may assume, under different sets of circumstances, as at high and low temperatures, two different crystalline forms, in which case it is said to be *dimorphous*. Sulphur and carbon furnish, as already

and, examples of this curious fact; another case is presented by calcium carbonate in the two modifications of calc spar and arragonite, both chemically the same, but physically different. A fourth example might be given of arsenic iodide, which also has two distinct forms, and even two distinct colors, offering as great a contrast as those of diamond and graphite.

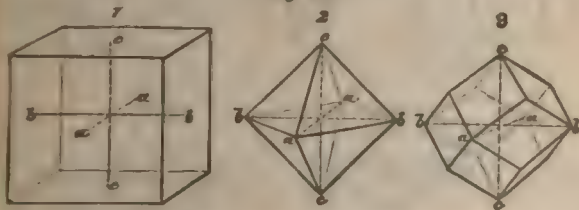
Crystallographic Systems.—When a crystal of simple form is carefully considered, it becomes evident that certain directions can be laid out in which straight lines may be imagined to be drawn, passing through the central point of the crystal from side to side, from end to end, from one angle to that opposed to it, etc., about which lines the particles either composing the crystal may be conceived to be symmetrically built. Such lines, or *axes*, are not always purely imaginary, however, as may be inferred from the remarkable optical properties of many crystals: their number, relative lengths, position, and inclination to each other, make the outward figure of the crystal itself.

Crystalline forms may upon this plan be arranged in six classes or systems; these are the following.

The monometric, regular, or cubic system (fig. 130).—The crystals of this division have three equal axes, all placed at right angles to each other. The most important forms are the cube (1), the regular octahedron (2), and the rhombic dodecahedron (3).

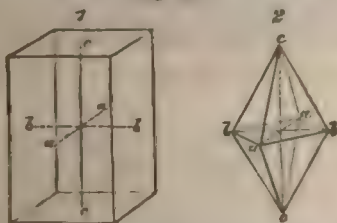
The letters $a=a$, $b=b$, $c=c$ (fig. 130) show the termination of the three axes, placed as stated.

Fig. 130.



By many substances, both simple and compound, assume these forms, and of the metals, carbon in the state of diamond, common salt, potassium chloride, the alums, fluor-spar, iron bisulphide, garnet, spinelle, etc.

Fig. 131.



The dimetric, quadratic, square prismatic, or pyramidal system.—The crystals of this system (fig. 131) are also symmetrical about three axes at right angles to each other. Of these, however, two only are

of equal length, the third, c — c , being longer or shorter. The most important forms are, the *right square prism* (1), and the *right square-based octahedron* (2).

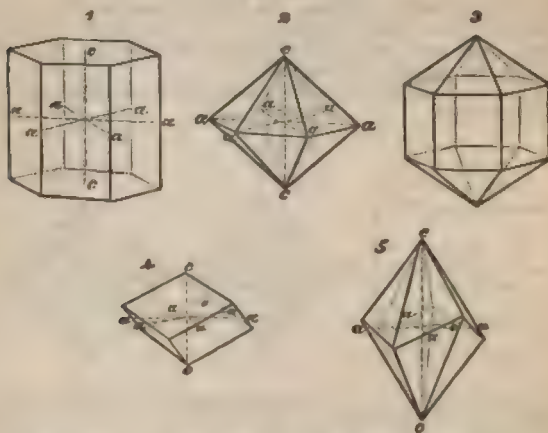
Examples of these forms are to be found in zircon, native stannic oxide, apophyllite, yellow potassium ferrocyanide, etc.

3. The rhombohedral system (fig. 132).—This is very important and extensive; it may be characterized by *four axes*,* three of which are equal, in the same plane, and inclined to each other at angles of 60° , while the fourth or principal axis is perpendicular to them all. The principal forms are,—the *regular six-sided prism* (1), the *regular double six-sided pyramid* (2), the *rhombohedron* (4), and the *scalenehedron* (5), a figure bounded by twelve scalene triangles.

Examples are found in ice, calcspar, sodium nitrate, beryl, quartz or rock-crystal, and the semi-metals, arsenic, antimony, and tellurium.

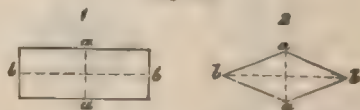
A combination of the regular six-sided prism and double six-sided pyramid (3) is a common form of quartz.

Fig. 132.



4. The trimetric, rhombic, or right prismatic system.—This is characterized by three axes of unequal lengths, placed at right angles to each other, as in the *right rectangular prism*, the *right rhombic prism*, the *right rectangular-based octohedron*, and the *right rhombic-based octohedron*.

Fig. 133.



The bases of these forms are represented in fig. 133 (1 and 2). Let the reader imagine a straight line passing through the centre of each of

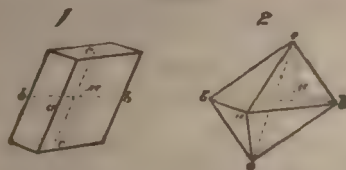
* This reference to four axes is a mere matter of convenience; three axes are sufficient for the determination of any solid figure whatever.

... iron pyrites, potassium nitrate and sulphate, barium sul-
phate.

The monoclinic or oblique prismatic system.—Crystals belonging to this group have also three axes, which may be all unequal; two of (the secondary) are placed at right angles, the third being so inclined as to be oblique to one and perpendicular to the other. To this system may be added the four following forms: The *oblique rectangular prism*, the *oblique rhombic prism*, the *oblique rectangular-based octahedron*, the *oblique rhombic-based octahedron*.

The bases of these monoclinic forms are identical in form with those of the triclinic system, fig. 133 (1) and (2). The principal axis may be represented by a line passing through the plane of the paper at the middle point, perpendicular to $a a$, and oblique to $b b$. The perspective forms are given in fig. 134.

Fig. 134.



These forms are taken by sulphur crystallized by fusion and cooling, by iron sulphate, carbonate and phosphate of sodium, borax, green vitriol, and many other salts.

The triclinic, anorthic, or doubly oblique prismatic system. Crystalline forms comprehended in this division are, from their great irregularity, exceedingly difficult to study and understand. In these are traced three axes, which may be all unequal in length, and are

the production of small triangular planes, which, as the process advances, gradually usurp the whole of the surface of the crystal, and convert the cube into an octohedron. The new planes are called *secondary*, and their production is said to take place by regular *decrements* upon the solid angles. The same thing may happen on the edges of the cube; a new figure, the

Fig. 135.



Passage of cube to octohedron.

rhombic dodecahedron, is then generated. The modifications which can thus be produced of the original or *primary* figure (all of which are subject to exact geometrical laws) are very numerous. Several distinct modifications may be present at the same time, and thus render the form exceedingly complex.

Crystals often cleave parallel to all the planes of the primary figure, as in calcspar, which offers a good illustration of this perfect cleavage. Sometimes one or two of these planes have a kind of preference over the rest in this respect, the crystal splitting readily in these directions only.

A very curious modification of the figure sometimes occurs by the excessive growth of each alternate plane of the crystal; the rest become at

Fig. 136.



Passage of octohedron to tetrahedron.

length obliterated, and the crystal assumes the character called *hemihedral* or *half-sided*. This is well seen in the production of the tetrahedron from the regular octohedron (fig. 136), and of the rhombohedral form by a similar change from the double six-sided pyramid (fig. 132, 2).

Forms belonging to the same crystallographic system are related to each other by several natural affinities.

1. *It is only the simple forms of the same system that can combine into a complex form.*—For in all fully developed (holohedral) natural crystals, it is found that all the similar parts, if modified at all, are modified in an exactly similar manner (in hemihedral forms, half the similar edges and angles alternately situated are similarly modified). Now this can be the case only when the dominant form and the modifying form are developed according to the same law of symmetry. Thus, if a cube and a regular octohedron are developed round the same system of axes, each summit of the cube is cut off to the same extent by a face of the octohedron, or *vice versa*. But a cube could never combine in this manner with a rhombic octohedron, because it would be impossible to place the two forms in such a manner that similar parts of the one should throughout replace similar parts of the other.

The crystals of each system are thus subject to a peculiar and distinct set of modifications, the observation of which very frequently constitutes an excellent guide to the discovery of the primary form itself.

2. *Crystals belonging to the same system are intimately related in their optical properties.*—(Crystals belonging to the regular system (as the diamond, rock-salt, etc.) refract light in the same manner as uncrystallized bodies, that is to say, they have but one refractive index, and a ray of light passing through them in any direction is refracted singly. But all the crystals refract doubly, that is to say, a ray of light passing through them (except in certain directions) is split into two rays, the one called the ordinary ray, being refracted as it would be by an amorphous body, the other, called the extraordinary ray, being refracted according to peculiar and more complex laws (see LIGHT). Now, the crystals of the trimetric and hexagonal systems resemble each other in this respect that in all of them there is one direction, called the optic axis, or line of double refraction (coinciding with the principal crystallographic axis) along which a ray of light is refracted singly, while in all other directions it is refracted doubly; whereas, in crystals belonging to the other systems, viz., the trimetric and the two oblique systems, there are always two directions or axes, along which a ray is singly refracted.

3. *Crystals belonging to the same system resemble each other in their mode of conducting heat.*—Amorphous bodies and crystals of the regular system conduct heat equally in all directions, so that, supposing a centre of heat to exist within such a body, the isothermal surfaces will be spheres. But crystals of the dimetric and hexagonal systems conduct equally only in directions perpendicular to the principal axis, so that in such crystals the isothermal surfaces are ellipsoids of revolution round that axis; and crystals belonging to either of the three other systems conduct unequally in all directions, so that in them the isothermal surfaces are ellipsoids with three unequal axes.

Relations of Form and Constitution; Isomorphism.

Certain substances, to which a similar chemical constitution is ascribed, possess the remarkable property of exactly replacing each other in crystallized compounds, without alteration of the characteristic geometrical figure. Such bodies are said to be *isomorphous*.*

For example, magnesia, zinc oxide, cupric oxide, ferrous oxide, and nickel oxide, are allied by isomorphic relations of the most intimate nature. The salts formed by these substances with the same acid and similar proportions of water of crystallization, are identical in their form, and, when of the same color, cannot be distinguished by the eye: the sulphates of magnesium and zinc may be thus confounded. These sulphates, too, all combine with potassium sulphate and ammonia sulphate, giving rise to double salts, whose figure is the same, but quite different from that of the simple sulphates. Indeed this connection between identity of form and parallelism of constitution runs through all their combinations.

In the same manner alumina and iron sesquioxide replace each other continually without change of crystalline figure: the same remark may be made of the oxides of potassium, sodium, ammonium. The alumina in common alum may be replaced by iron sesquioxide, the potash by ammonia or by soda, and still the figure of the crystal remains unchanged. These replacements may be partial only: we may have an alum containing both potash and ammonia, or alumina and chromium sesquioxide. By artificial management—namely, by transferring the crystal successively to

* From *isos*, equal, and *morphos*, shape or form.

different solutions—we may have these isomorphous and mutually replacing compounds distributed in different layers upon the same crystal.

For these reasons mixtures of isomorphous salts can never be separated by crystallization, unless their difference of solubility is very great. A mixed solution of ferrous sulphate and nickel sulphate, isomorphous salts, yields on evaporation crystals containing both iron and nickel. But if before evaporation the ferrous salt be converted into ferric salt, by chlorine or other means, then the crystals obtained are free from iron, except that of the mother-liquor which wets them. The ferric salt is no longer isomorphous with the nickel salt, and easily separates from the latter.

Absolute identity of value in the angles of crystals is not always exhibited by isomorphous substances. In other words, small variations often occur in the magnitude of the angles of crystals of compounds which in all other respects show the closest isomorphic relations. This should occasion no surprise, as there are reasons why such variations might be expected, the chief perhaps being the unequal effects of expansion by heat, by which the angles of the same crystal are changed by alteration of temperature. A good example is found in the case of the carbonates of calcium, magnesium, manganese, iron, and zinc, which are found native crystallized in the form of obtuse rhombohedrons (fig. 132, 4), not distinguishable from each other by the eye, but exhibiting small differences in their angles when accurately measured. These compounds are isomorphous, and the measurements of the obtuse angles of their rhombohedrons are as follows:—

| | | |
|-------------------|-----------|----------|
| Calcium carbonate | | 105° 5' |
| Magnesium " | | 107° 25' |
| Manganese " | | 107° 20' |
| Ferrous " | | 107° |
| Zinc " | | 107° 40' |

Anomalies in the composition of various earthy minerals, which formerly threw much obscurity upon their chemical nature, have been in great measure explained by these discoveries. Specimens of the same mineral from different localities were found to afford very discordant results on analysis. But the proof once given of the extent to which substitution of isomorphous bodies may go, without destruction of what may be called the primitive type of the compound, these difficulties vanish.

Decision of a doubtful point respecting the constitution of a compound may sometimes be very satisfactorily made by reference to its isomorphous relations, as in the case of alumina, already mentioned, which is isomorphous with the sesquioxide of iron (p. 227).

The direct determination of the crystalline forms of the elementary bodies is often difficult, and the question of their isomorphism is complicated by the frequent dimorphism which they exhibit, but when compounds are found to correspond in chemical constitution and crystalline form, it may sometimes be inferred that the elements composing them are likewise isomorphous. Thus, the metals magnesium, zinc, iron, and copper are presumed to be isomorphous. Arsenic and phosphorus have not the same crystalline form; nevertheless they are said to be isomorphous, because arsenic and phosphoric acids give rise to combinations which agree most completely in figure and constitution. The chlorides, iodides, bromides, and fluorides agree, whenever they can be observed, in the most perfect manner: hence the elements themselves are believed to be isomorphous.

The subjoined table, taken with slight modification from Graham's

"Elements of Chemistry,"* will serve to convey some idea of the most important families of isomorphous elements:—

Isomorphous Groups.

| | | |
|------------|------------|------------|
| (1) | (3) | (6) |
| Sulphur | Barium | Sodium |
| Selenium | Strontium | Silver |
| Tellurium. | Lead. | Thallium |
| | | Gold |
| (2) | (4) | Potassium |
| Magnesium | Platinum | Ammonium. |
| Calcium | Iridium | |
| Manganese | Osmium. | (7) |
| Iron | | Chlorine |
| Cobalt | (5) | Iodine |
| Nickel | Tin | Bromine |
| Zinc | Titanium | Fluorine |
| Caesium | Zirconium | Cyanogen. |
| Copper | Tungsten | |
| Chromium | Molybdenum | (8) |
| Aluminium | Tantalum | Phosphorus |
| Glucinum. | Niobium. | Arsenic |
| | | Antimony |
| | | Bismuth |
| | | Vanadium. |

A comparison of this table with that on page 239 will show that in many cases, isomorphous elements exhibit equal quantivalence or combining capacity, and more generally that the isomorphous groups consist wholly or wholly of triad elements. The only apparent exception to the rule is afforded by tantalum and niobium, which, although pentads, are isomorphous with tin, tungsten, and other tetrad and hexad elements.

* Second edition, vol. 1. p. 175.

CHEMICAL AFFINITY.

THE term Chemical Affinity, or Chemical Attraction, is used to describe that particular power or force, in virtue of which, union, often of a very intimate and permanent nature, takes place between two or more bodies, in such a way as to give rise to a *new* substance, having, for the most part, properties completely in discordance with those of its components.

The attraction thus exerted between different kinds of matter is to be distinguished from other modifications of attractive force which are exerted indiscriminately between all descriptions of substances, sometimes at enormous distances, sometimes at intervals quite inappreciable. Examples of the latter are to be seen in cases of what is called *cohesion*, when the particles of solid bodies are immovably bound together into a mass. Then there are other effects of, if possible, a still more obscure kind; such as the various actions of surface, the adhesion of certain liquids to glass, the repulsion of others, the ascent of water in narrow tubes, and a multitude of curious phenomena which are described in works on Physics, under the head of *molecular actions*. From all these, true chemical attraction may be at once distinguished by the deep and complete change of characters which follows its exertion: we might indeed define affinity to be a force by which new substances are generated.

It seems to be a general law that bodies most opposed to each other in chemical properties evince the greatest tendency to enter into combination; and, conversely, bodies between which strong analogies and resemblance can be traced manifest a much smaller amount of mutual attraction. For example, hydrogen and the metals tend very strongly indeed to combine with oxygen, chlorine, and iodine, but the attraction between the different members of these two groups is comparatively feeble. Sulphur and phosphorus stand, as it were, midway: they combine with substances of one and the other class, their properties separating them sufficiently from both. Acids are drawn towards alkalis, and alkalis towards acids, while union among themselves rarely if ever takes place.

Nevertheless, chemical combination graduates so imperceptibly into mere mechanical mixture, that it is often impossible to mark the limit. Solution is the result of a weak kind of affinity existing between the substance dissolved and the solvent—an affinity so feeble as completely to lose one of its most prominent features when in a more exalted condition—namely, power of causing elevation of temperature: for in the act of mere solution, the temperature falls, the heat of combination being lost and overpowered by the effects of change of state.

The force of chemical attraction thus varies greatly with the nature of the substances between which it is exerted; it is influenced, moreover, to a very large extent, by external or adventitious circumstances. An idea formerly prevailed that the relations of affinity were fixed and constant between the same substances, and great pains were taken in the preparation of tables exhibiting what was called the precedence of affinities. The order pointed out in these lists is now acknowledged to represent the order of precedence *for the circumstances* under which the experiments were made, but nothing more; so soon as these circumstances become changed, the order is disturbed. The ultimate effect, indeed, is not the result of the exercise of one single force, but rather the joint effect of a number, so complicated and so variable in intensity, that, in the greater number of cases, *it is not possible to predict the consequences of a yet untried experiment.*

It will be proper to examine shortly some of these extraneous causes to which allusion has been made, which modify to so great an extent the direct and original effects of the specific attractive force.

Alteration of temperature may be reckoned among these. When metallic mercury is heated nearly to its boiling point, and in that state exposed for a long time to the air, it absorbs oxygen, and becomes converted into a red crystalline powder. This very same substance, when raised to a still higher temperature, separates spontaneously into metallic mercury and oxygen gas. It may be said, and probably with truth, that the latter change is greatly aided by the tendency of the metal to assume the vaporous state, but precisely the same fact is observed with another metal, palladium, which is not volatile, excepting at extremely high temperatures, and which oxidizes superficially at a red heat, and again becomes reduced when the temperature rises to whiteness.

Volatility and the power of vaporization are, perhaps, beyond all other disposing causes, the most potent; they interfere in almost every reaction which takes place, and very frequently turn the scale when the opposed forces do not greatly differ in energy. It is easy to give examples. When a solution of calcium chloride is mixed with a solution of ammonium carbonate, double interchange ensues, calcium carbonate and ammonium chloride being generated: $\text{CaCl}_2 + (\text{NH}_4)_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NH}_4\text{Cl}$. Here the scale can be shown to be in a great measure determined by the insolubility of the calcium carbonate. On the other hand, when dry calcium carbonate is powdered and mixed with ammonium chloride, and the whole heated in a retort, a sublimate of ammonium carbonate is formed, while calcium chloride remains behind. In this instance, it is no doubt the great volatility of the new ammoniacal salt which chiefly determines the kind of decomposition.

When iron filings are heated to redness in a porcelain tube, and vapor of water is passed over them, the water undergoes decomposition with the easiest facility, hydrogen being rapidly disengaged, and the iron converted into oxide. On the other hand, oxide of iron, heated in a tube through which a stream of dry hydrogen is passed, suffers almost instantaneous reduction to the metallic state, while the vapor of water, carried forward by the current of gas, escapes as a jet of steam from the extremity of the tube. In these experiments, the affinities between the iron and oxygen and the hydrogen and oxygen are so nearly balanced, that the difference is scarcely sufficient to settle the point. An atmosphere of steam offers little resistance to the escape of hydrogen; an atmosphere of hydrogen offers the same relation to steam; and this apparently trifling difference of circumstances is quite enough for the purpose.

What is called the *nascent state* is one very favorable to chemical combination. Thus, nitrogen refuses to combine with gaseous hydrogen; yet, when these substances are simultaneously liberated from some previous combination, they unite with great ease, as when organic matters are decomposed by heat, or by spontaneous putrefactive change.

There is a remarkable, and, at the same time, very extensive class of cases, grouped together under the general title of cases of *disposing affinity*. Metallic silver does not oxidize at any temperature: nay, more, its oxide is easily decomposed by simple heat; yet, if the finely-divided metal be mixed with siliceous matter and alkali, and ignited, the whole fuses to a yellow transparent glass of silver silicate. Platinum is attacked by fused potassium hydrate, hydrogen being probably disengaged while the metal is oxidized: this is an effect which never happens to silver under the same circumstances, although silver is a much more oxidizable substance than platinum. The fact is, that potash forms with the oxide of the last-named metal a kind of *saline compound*, in which the platinum oxide acts as an

acid; and hence its formation under the *disposing* influence of the powerful base.

In the remarkable decompositions suffered by various organic bodies when heated in contact with caustic alkali or lime, we have other examples of the same fact. Products are generated which are never formed in the absence of the base; the reaction is invariably less complicated, and its results fewer in number and more definite, than in the event of simple destruction by a graduated heat.

There is yet a still more obscure class of phenomena, called *catalytic*, in which effects are brought about by the mere *presence* of a substance which itself undergoes no perceptible change: the experiment mentioned in the chapter on oxygen, in which that gas is obtained, with the greatest facility, by heating a mixture of potassium chlorate and manganese dioxide, is a case in point. The salt is decomposed at a very far lower temperature than would otherwise be required, and yet the manganese oxide does not appear to undergo any alteration, being found after the experiment in the same state as before. It may, however, undergo a temporary alteration. We know, indeed, that this oxide when in contact with alkalies, is capable of taking up an additional proportion of oxygen and forming manganic acid; and it is quite possible that in the reaction just considered it may actually take oxygen from the potassium chlorate, and pass to the state of a higher oxide, which, however, is immediately decomposed, the additional oxygen being evolved, and the dioxide returning to its original state. The same effect in facilitating the decomposition of the chlorate is produced by cupric oxide, ferric oxide, and lead oxide, all of which are known to be susceptible of higher oxidation. The oxides of zinc and magnesium, on the contrary, which do not form higher oxides, are not found to facilitate the decomposition of the chlorate; neither is any such effect produced by mixing the salt with other pulverulent substances, such as pounded glass or pure silica.

The so-called catalytic actions are often mixed up with other effects which are much more intelligible, as the action of finely divided platinum on certain gaseous mixtures, in which the solid appears to condense the gas upon its greatly extended surface, and thereby to induce combination by bringing the particles within the sphere of their mutual attractions.

Influence of Pressure on Chemical Action.—When a body is decomposed by heat in a confined space, and one or more of the separated elements (ultimate or proximate) is gaseous, the decomposition goes on until the liberated gas or vapor has attained a certain tension, greater or less according to the temperature. So long as this temperature remains constant, no further decomposition takes place, neither does any portion of the separated elements recombine: but if the temperature be raised, decomposition recommences, and goes on till the liberated gas or vapor has attained a certain higher tension, also definite for that particular temperature; if on the other hand the temperature be lowered, recombination takes place, until the tension of the remaining gas is reduced to that which corresponds with the lower temperature. These phenomena, which are closely analogous to those exhibited in the vaporization of liquids, have been especially studied by Deville and Debray.* Deville designates decomposition under these conditions by the term "Dissociation."

When *calcium carbonate* is heated in an iron tube, from which the air has been exhausted by means of a mercury-pump, no decomposition takes place at 300°, and a scarcely perceptible decomposition at 440°; but at 800° (in vapor of cadmium) it becomes very perceptible, and goes on till

* *Watts's Dictionary of Chemistry*, first Supplement, p. 425.

the tension of the evolved carbon dioxide becomes equivalent to 85 millimetres of mercury; there it stops so long as the temperature remains constant; but on raising the temperature to 1040° (in vapor of zinc) more carbon dioxide is evolved until a tension equivalent to about 520 mm. is attained. If the tension be reduced by working the pump, it is soon restored to its former value by a fresh evolution of carbon dioxide. If, on the other hand, the apparatus be allowed to cool, the carbon dioxide is gradually resorbed by the quicklime, and a vacuum is re-established in the apparatus.

Similar phenomena are exhibited in the efflorescence of hydrated salts, and in the decomposition of the compounds of ammonia with metallic chlorides, in closed spaces.

If the decomposed body, as well as one at least of its constituents, is gaseous, it is not possible to obtain an exact measurement of the maximum tension corresponding with the temperature; nevertheless the decomposition is found to take place according to the same general law, ceasing as soon as the liberated gases have obtained a certain tension, which is greater as the temperature is higher.

It has long been known that chemical combination between any two bodies capable of uniting directly, takes place only at and above a certain temperature, and that the combination is broken up at a higher temperature; but it is only in later years that we have become acquainted with the fact that bodies like water begin to decompose at temperatures considerably below that which they produce in the act of combining, and therefore that their combination at that temperature is never complete. We have showed some years ago that water is resolved into its elements in contact with intensely ignited platinum. This reaction has been more closely studied by Deville, who finds that when vapor of water is passed through a heated platinum tube, decomposition commences at 960° – 1000° (about the melting point of silver), but proceeds only to a limited extent; on raising the temperature to 1200° , further decomposition takes place, but again only to a limited amount, ceasing in fact as soon as the liberated oxygen and hydrogen have attained a certain higher tension. The quantity of these gases actually collected in this experiment is, however, very small, the greater portion of them recombining as they pass through the cooler part of the apparatus, till the tension of the remainder is reduced to that which corresponds with the lower temperature.

The recombination of the gases may be prevented to a certain extent by means of an apparatus consisting of a wide tube of glazed earthen-ware, through the axis of which passes a narrower tube of porous earthen-ware, the two being tightly fitted by perforated corks provided with gas-delivery tubes, and the whole strongly heated by a furnace. Vapor of water is passed through the inner tube, carbon dioxide through the annular space between the two, and the gases, after passing through the heated tubes, are received over caustic potash-solution. The vapor of water is then decomposed by the heat as before; but the hydrogen, according to the laws of diffusion, passes through the porous earthen-ware into the surrounding atmosphere of carbon dioxide, being thus separated from the oxygen, which remains in the inner tube, and becomes mixed with carbon dioxide passing through the porous septum in the opposite direction to the hydrogen. As these gases pass through the alkaline water, the carbon dioxide is absorbed, and a mixture of hydrogen and oxygen collects in the receiver. A gram of water passed in the state of vapor through such an apparatus yields about a cubic centimetre of detonating gas.

The retarding influence of pressure is seen also in the action of acids upon zinc, or the electrolysis of water, in sealed tubes. In these cases the elimination of a gas is an essential condition of the change, and this

being prevented, the action is retarded. On the other hand, there are numerous reactions which are greatly promoted by increased pressure—those, namely, which depend on the solution of gases in liquids, or on the prolonged contact of substances which under ordinary pressure would be volatilized by heat.

Relations of Heat to Chemical Affinity.—Whatever may be the real nature of chemical affinity, one most important fact is clearly established with regard to it; namely, that its manifestations are always accompanied by the production or annihilation of heat. Change of composition, or chemical action, and heat are mutually convertible: a given amount of chemical action will give rise to a certain definite amount of heat, which quantity of heat must be directly or indirectly expended, in order to reverse or undo the chemical action that has produced it. The production of heat by chemical action, and the definite quantitative relation between the amount of heat evolved and the quantity of chemical action which takes place, are roughly indicated by the facts of our most familiar experience; thus, for instance, the only practically important method of producing heat artificially consists in changing the elements of wood and coal, together with atmospheric oxygen, into carbon dioxide and water; and every one knows that the heat thus obtainable from a given quantity of coal is limited, and is, at least approximately, always the same. The accurate measurement of the quantity of heat produced by a given amount of chemical action is a problem of very great difficulty; chiefly because chemical changes very seldom take place alone, but are almost always accompanied by physical changes, involving further calorimetric effects, each of which requires to be accurately measured and allowed for, before the effect due to the chemical action can be rightly estimated. Thus the ultimate result has, in most cases, to be deduced from a great number of independent measurements, each liable to a certain amount of error. It is, therefore, not surprising that the results of various experiments should differ to a comparatively great extent, and that some uncertainty should still exist as to the exact quantity of heat corresponding with even the simplest cases of chemical action.

The experiments are made by inclosing the acting substances in a vessel called a calorimeter, surrounded by water or mercury, the rise of temperature in which indicates the quantity of heat evolved by the chemical action, after the necessary corrections have been made for the heat absorbed by the containing vessel and the other parts of the apparatus, and for the amount lost by radiation, etc. Combustions in oxygen and chlorine are made in a copper vessel surrounded by water; the heat evolved by the mutual action of liquids or dissolved substances is estimated by means of a smaller calorimeter containing mercury. The construction of these instruments and the methods of observation involve details which are beyond the limits of this work.*

The following table gives the quantities of heat, expressed in heat-units,† evolved in the combustion of various elements, and a few compounds, in oxygen, referred: (1) to 1 gram of each substance burned; (2) to 1 gram of oxygen consumed; (3) to one atom or molecule (expressed in grams), of the various substances:—

* See Müller's *Chemical Physics*, pp. 338, *et seq.*, and Watts's *Dictionary of Chemistry*, iii. 28, 103.

† The unit of heat here adopted is the quantity of heat required to raise 1 gram of water from 0° to 1° C.

Heat of Combustion of Elementary Substances in Oxygen.

| Substance. | Product. | Units of heat evolved. | | | Observer. |
|-----------------------|--------------------------------|-------------------------|----------------------|------------------------|-----------------------------|
| | | By 1 gram of substance. | By 1 gram of oxygen. | By 1 at. of substance. | |
| Hydrogen . . . | H ₂ O | { 33881
34462 | 4235
4308 | 33881
34462 | Andrews.
Favre & Silber- |
| Carbon— | | | | | [mann. |
| Wood-charcoal . . | CO ₂ | { 7900
8080 | 2962
3030 | 94800
96960 | Andrews.
Favre & Silber- |
| Gas-retort carbon . | " | 8047 | 3018 | 96564 | " [mann. |
| Native graphite . . | " | 7797 | 2924 | 93564 | " |
| Artificial graphite . | " | 7762 | 2911 | 93144 | " |
| Diamond . . . | " | 7770 | 2914 | 93940 | " |
| Sulphur— | | | | | |
| Native . . . | SO ₂ | 2220 | 2220 | 71040 | " |
| Recently melted . . | " | 2260 | 2260 | 72320 | " |
| Flowers . . . | " | 2307 | 2307 | 73821 | Andrews. |
| Phosphorus— | | | | | |
| (Yellow) . . . | P ₂ O ₅ | 5747 | 4454 | 178157 | " |
| Zinc . . . | ZnO | 1330 | 5390 | 86450 | " |
| Iron . . . | Fe ₂ O ₃ | 1582 | 4153 | 88592 | " |
| Tin . . . | SnO ₂ | 1147 | 4230 | 135360 | " |
| Copper . . . | CuO | 603 | 2394 | 38394 | " |

The following results have been obtained by the complete combustion of partially oxidized substances:—

| Substance. | Product. | Units of heat evolved. | | Observer |
|----------------------------------|------------------|-------------------------|---|--|
| | | By 1 gram of substance. | In formation of 1 molecule of the ultimate product. | |
| Carbon monoxide, CO . . . } | CO ₂ | { 2403
2431 | 67284
68064 | { Favre & Sil-
bermann.
Andrews. |
| Stannous oxide, SnO | SnO ₂ | 519 | 69584 | " |
| Cuprous oxide, Cu ₂ O | CuO | 256 | 18304 | " |

The last three substances in this table contain exactly half as much oxygen as the completely oxidized products: and on comparing the amount of heat evolved in the formation of one molecule of stannic or cupric oxide from the corresponding lower oxide, with the quantity produced when a molecule of the same product is formed by the complete oxidation of the metal in one operation, we find that the combination of the second half of the oxygen contained in these bodies evolves sensibly half as much as the combination of the whole quantity. In the formation of carbon dioxide,

however, the second half of the oxygen appears to develop more than two-thirds of the total amount of heat; but this result is probably due, in part at least, to the fact that when carbon is burned into carbon dioxide, a considerable but unknown quantity of heat is expended in converting the solid carbon into gas, and thus escapes measurement; while, in carbon monoxide, the carbon already exists in the gaseous form, and therefore no portion of the heat evolved in the combustion of this substance is similarly expended in producing a change of state.

It seems probable, also, that a similar explanation may be given of the inequalities in the quantities of heat produced by the combustion of different varieties of pure carbon and of sulphur—that is to say, that a portion of the heat generated by the combustion of diamond and graphite goes to assimilate their molecular condition to that of wood-charcoal, and that there is an analogous expenditure of heat in the combustion of native sulphur.

The quantities of heat evolved in the combination of chlorine, bromine, and iodine with other elements have been determined by Favre and Silbermann, Andrews, and others; but we must refer to larger works for the results.*

Reactions in Presence of Water.—The thermal effects which may result from the reaction of different substances on one another in presence of water, are more complicated than those resulting from direct combination. In addition to the different specific heats of the re-agents and products, and to the different quantities of heat absorbed by them in dissolving, or given out by them in combining with water, the conversion of soluble substances into insoluble ones, as a consequence of the chemical action, or the inverse change of insoluble into soluble bodies, are among the secondary causes to which part of the calorimetric effect may be due in these cases.

When a gas dissolves in water, the heat due to the chemical action is augmented by that due to the liquefaction of the gas; so also when a solid body is dissolved in water, the total thermal effect is due in part to the chemical action taking place between the water and the solid, and in part to the liquefaction of the substance dissolved. In the former case the chemical and physical parts of the phenomena both cause evolution of heat; in the latter case the physical change occasions disappearance of heat, and if this effect is greater than that due to the chemical action, the ultimate effect is the production of cold, and it is this which is generally observed.

Cold produced by Chemical Decomposition.—It is highly probable that the thermal effect of the reversal of a given chemical action is in all cases equal and opposite to the thermal effect of that action itself. A direct consequence of this proposition is that *the separation of any two bodies is attended with the absorption of a quantity of heat equal to that which is evolved in their combination.* The truth of this deduction has been experimentally established in various cases, by Wood,† Joule,‡ and Favre and Silbermann, by comparing the heat evolved in the electrolysis of dilute sulphuric acid, or solutions of metallic salts, with that which is developed in a thin metallic wire by a current of the same strength: also by comparison of the heat evolved in processes of combination accompanied by simultaneous decomposition, with that evolved when the same combination occurs between free elements.

By determining the heat evolved when different metals were dissolved

* *Watts's Dictionary of Chemistry*, iii. 109.

† *Phil. Mag.* [1] (1. 308; 1v. 370).

‡ *Ibid* iii. 481.

in water or dilute acid, Wood found that it was less than that which would be produced by the direct oxidation of the same metals, by a quantity equal to that which would be obtained by burning the hydrogen set free, or which was expended in decomposing the water or acid; and, therefore, that when this latter quantity was added to the results, they agreed with the numbers given by experiments of direct oxidation.

ELECTRO-CHEMICAL DECOMPOSITION; CHEMISTRY OF THE VOLTAIC PILE.

When a voltaic current of considerable power is made to traverse various compound liquids, a separation of the elements of these liquids ensues: provided that the liquid be capable of conducting the current, its decomposition almost always follows.

The elements are disengaged solely at the limiting surfaces of the liquid, where, according to the common mode of speech, the current enters and leaves the latter, all the intermediate portions appearing perfectly quiescent. In addition, the elements are not separated indifferently and at random at these two surfaces; but, on the contrary, make their appearance with perfect uniformity and constancy at one or the other, according to their chemical character, namely, oxygen, chlorine, iodine, acids, etc., at the surface connected with the *copper*, or *positive* end of the battery; hydrogen, the metals, etc., at the surface in connection with the *zinc*, or *negative* extremity of the arrangement.

The terminations of the battery itself—usually, but by no means necessarily, of metal—are designated poles or *electrodes*,* as by their intervention the liquid to be experimented on is made a part of the circuit. The process of decomposition by the current is called *electrolysis*,† and the liquids which, when thus treated, yield up their elements, are denominated *electrolytes*.

When a pair of platinum plates are plunged into a glass of water to which a few drops of oil of vitriol have been added, and the plates connected by wires with the extremities of an active battery, oxygen is disengaged at the positive electrode, and hydrogen at the negative, in the proportion of one measure of the former to two of the latter nearly. This experiment has already been described.‡

A solution of hydrochloric acid mixed with a little Saxon blue (indigo), and treated in the same manner, yields hydrogen on the negative side and chlorine on the positive, the indigo there becoming bleached.

Potassium iodide dissolved in water is decomposed in a similar manner: the free iodine at the positive side can be recognized by its brown color, or by the addition of a little gelatinous starch.

All liquids are not electrolytes; many refuse to conduct, and no decomposition can then occur; alcohol, ether, numerous essential oils, and other products of organic chemistry, besides a few saline inorganic compounds, act in this manner, and completely arrest the current of a powerful battery.

One of the most important and indispensable conditions of electrolysis

* From *ἑκτρος*, and *δρε*, a way.

† From *ἑκτρος*, and *λύω*, to loose.

‡ Page 137.

is fluidity; bodies which, when reduced to the liquid state, conduct freely, and as freely suffer decomposition, become insulators to the electricity of the battery when they become solid. Lead chloride offers a good illustration of this fact: when fused in a porcelain crucible, it gives up its elements with the utmost ease, and a galvanometer, interposed in the circuit, is strongly affected. But, when the source of heat is withdrawn, and the salt suffered to solidify, signs of decomposition cease, and at the same moment the magnetic needle reassumes its natural position. In the same manner, the thinnest film of ice arrests the current of a powerful voltaic apparatus; but the instant the ice is liquefied, so that water communication is restored between the electrodes, the current again passes, and decomposition occurs. Fusion by heat, and solution in aqueous liquids, answer the purpose equally well.

Generally speaking, compound liquids cannot conduct the electric current without being decomposed; but still there are a few exceptions to this statement, which perhaps are more apparent than real. Thus, Hittorf has shown that fused silver sulphide, which was formerly regarded as one of the exceptions, cannot be considered to be so, and Beetz has since proved the same to be the case as regards mercuric iodide and lead fluoride.

The quantity of any given compound liquid which can be decomposed by any given electric battery, depends on the resistance of the liquid: the more resistance, the less decomposition. Distilled water has only a small power of conduction, and is therefore only slightly decomposed by a battery of 30 to 40 pairs; whilst diluted sulphuric acid is one of the best of fluid conductors, and undergoes rapid decomposition by a small battery.

When a liquid which can be decomposed, and a galvanometer, are included in the circuit of an electric current, if the needle of the galvanometer be deflected, it may be always assumed as certain that a portion of liquid, bearing a proportion to the strength of the current, is decomposed, although it may be impossible in many cases, without special contrivances, to detect the products of the decomposition, on account of their minuteness.

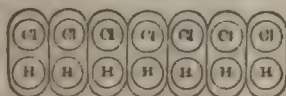
The metallic terminations of the battery, the poles or electrodes, have, in themselves, nothing in the shape of attractive or repulsive power for the elements separated at their surfaces. Finely-divided metal suspended in water, or chlorine held in solution in that liquid, shows not the least symptom of a tendency to accumulate around them; a single element is altogether unaffected—directly, at least; separation from previous combination is required, in order that this appearance should be exhibited.

It is necessary to examine the process of electrolysis a little more closely. When a portion of hydrochloric acid, for example, is subjected to decomposition in a glass vessel with parallel sides, chlorine is disengaged at the positive electrode, and hydrogen at the negative; the gases are perfectly pure and unmixed. If, while the decomposition is rapidly proceeding, the intervening liquid be examined by a beam of light, or by other means, not the slightest disturbance or movement of any kind will be perceived; nothing like currents in the liquid, or bodily transfer of gas from one part to another, can be detected; and yet two portions of hydrochloric acid, separated perhaps by an interval of four or five inches, may be respectively evolving pure chlorine and pure hydrogen.

There is, it would seem, but one mode of explaining this and all similar cases of regular electrolytic decomposition: this is by assuming that *all* the particles of hydrochloric acid between the electrodes, and by which the current is conveyed, simultaneously suffer decomposition, the hydrogen travelling in one direction, and the chlorine in the other. The neighboring elements, thus brought into close proximity, unite and reproduce hydrochloric acid, again destined to be decomposed by a repetition of the

same change. In this manner each particle of hydrogen may be made to travel in one direction, by becoming successively united to each particle of chlorine between itself and the negative electrode; when it reaches the latter, finding no disengaged particle of chlorine for its reception, it is rejected, as it were, from the series, and thrown off in a separate state. The same thing happens to each particle of chlorine, which at the same time passes continually in the opposite direction, by combining successively with each particle of hydrogen, that moment separated, with which it meets, until at length it arrives at the positive plate or wire, and is disengaged. A succession of particles of hydrogen is thus continually thrown off from the decomposing mass at one extremity, and a corresponding succession of particles of chlorine at the other. The power of the current is exerted with equal energy in every part of the liquid conductor,

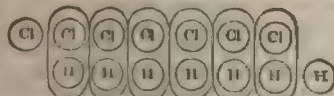
Fig. 137.



Hydrochloric acid in its usual state.

though its effects become manifest only at the very extremities. The action is one of a purely molecular or internal nature, and the metallic termina-

Fig. 138.



Hydrochloric acid undergoing electrolysis.

tions of the battery merely serve the purpose of completing the connection between the latter and the liquid to be decomposed. The figures 137 and 138 are intended to assist the imagination of the reader, who must at the same time avoid regarding them in any other light than that of a somewhat figurative mode of representing the phenomena described. The circles are intended to indicate the elements, and are distinguished by their respective symbols.

Like hydrochloric acid, all electrolytes, when acted on by electricity, are split into two constituents, which pass in opposite directions. Substances of the one class, like oxygen, chlorine, etc., are evolved at the positive electrode; those of the other class, like hydrogen and the metals, at the negative electrode.

It is of importance to remark that oxygen-salts, such as sulphates and nitrates, when acted on by the current, do not divide into acid and basic oxide, but, as Daniell and Miller proved, into metal and a compound substance, or group of elements, which is transferred in such a state of association that, as regards its electrical behavior, it represents an element. Thus, cupric sulphate, CuSO_4 , splits, not into SO_3 and CuO , but into metallic copper and sulphuric acid, SO_4 . Hydrogen sulphate, or sulphuric acid, H_2SO_4 , divides into the same compound group and hydrogen. In a similar way, also, the part of the electrolyte which passes to the negative pole may consist of a group of elements. A solution of sal-ammoniac, NH_4Cl , furnishes a beautiful instance of this fact, since it is decomposed by the current in such a manner that the ammonium, NH_4 , goes to the negative

pole, where it is resolved into ammonia, NH_3 , and free hydrogen, and the chlorine to the positive pole.

A distinction must be carefully drawn between true and regular electrolysis, and what is called secondary decomposition, brought about by the reaction of the bodies so eliminated upon the surrounding liquid, or upon the substance of the electrodes: hence the advantage of platinum for the latter purpose, when electrolytic actions are to be studied in their greatest simplicity, that metal being scarcely attacked by any ordinary agents. When, for example, a solution of lead nitrate or acetate is decomposed by the current between platinum plates, metallic lead is deposited at the negative side, and a brown powder, lead dioxide, at the positive: the latter substance is the result of a secondary action; it proceeds, in fact, from the nascent oxygen, at the moment of its liberation, reacting upon the monoxide of lead present in the salt, and converting it into dioxide, which is insoluble in the dilute acid. When nitric acid is decomposed, no hydrogen appears at the negative electrode, because it is oxidized at the expense of the acid, which is reduced to nitrous acid. When potassium sulphate, K_2SO_4 , is electrolyzed, hydrogen appears at the negative electrode, together with an equivalent quantity of potassium hydroxide, KHO , because the potassium which is evolved at the electrode immediately decomposes the water there present. At the same time, the sulphuric acid, SO_4 , which is transferred to the positive electrode, takes hydrogen from the water there present, forming sulphuric acid, H_2SO_4 , and liberating oxygen. In like manner hydrogen sulphate, or sulphuric acid itself, is resolved by the current into hydrogen and sulphuric acid, which latter decomposes the water at the positive electrode, reproducing hydrogen sulphate, and liberating oxygen, just as if the water itself were directly decomposed by the current into hydrogen and oxygen. A similar action takes place in the electrolytic decomposition of any other oxygen salt of an alkali-metal, or alkaline earth-metal, alkali and hydrogen gas making their appearance at the negative electrode, acid and oxygen gas at the positive electrode. This observation explains a circumstance which much perplexed the earlier experimenters upon the chemical action of the voltaic battery. In all experiments in which water was decomposed, both acid and alkali were liberated at the electrodes, even though distilled water was employed: and hence it was believed for some time that the voltaic current had some mysterious power of generating acid and alkaline matter. The true course of these compounds was, however, traced by Davy,* who showed that they proceeded from impurities either in the water itself, or in the vessels which contained it, or in the surrounding atmosphere. Having proved that ordinary distilled water always contains traces of saline matter, he redistilled it at a temperature below the boiling point, in order to avoid all risk of carrying over salts by splashing. He then found that when marble cups were used to contain the water used for decomposition, hydrochloric acid appeared at the positive electrode, soda at the negative, both being derived from sodium chloride present in the marble; when agate cups were used, he obtained silica; and when he used gold vessels, he obtained nitric acid and ammonia, which he traced to atmospheric air. By operating in a vacuum, indeed, the quantity of acid and alkali was reduced to a minimum, but the decomposition was almost arrested, although he operated with a battery of fifty pairs of 4-inch plates. Hence it is manifest that *water itself is not an electrolyte*, but that it is enabled to convey the current if it contains only traces of saline matter.†

Definite Chemical Action of the Electric Current.—If a number of different electrolytes, such as dilute sulphuric acid, cupric sulphate, potassium

* Philosophical Transactions, 1807.

† Mather's Chemical Physics, p. 66.

iodide, fused lead chloride, etc., be arranged in a series, and the same current be made to traverse the whole, all will suffer decomposition at the same time, but by no means to the same amount. If arrangements be made by which the quantities of the eliminated elements can be accurately ascertained, it will be found, when the decomposition has proceeded to some extent, that these latter have been disengaged exactly in the ratio of their chemical equivalents. The same current which decomposes 9 parts of water will separate into their elements 166 parts of potassium iodide, 139 parts of lead chloride, etc. Hence the very important conclusion: *The action of the current is perfectly definite in its nature, producing a fixed and constant amount of decomposition, expressed in each electrolyte by the value of its chemical equivalent.*

From a very extended series of experiments, based on this and other methods of research, Faraday was enabled to draw the general inference that effects of chemical decomposition are always proportionate to the quantity of circulating electricity, and may be taken as an accurate and trustworthy measure of the latter. Guided by this highly important principle, he constructed his *voltametre*, an instrument which has rendered the greatest service to electrical science. This is merely an arrangement by which dilute sulphuric acid is decomposed by the current, the gas evolved being collected and measured. By placing such an instrument in any part of the circuit, the quantity of electric force necessary to produce any given effect can be at once estimated; or, on the other hand, any required amount of the latter can be, as it were, measured out and adjusted to the object in view. The voltametre has received many different forms: one of the most extensively useful is that shown in fig. 139, in which the platinum plates are separated by a very small interval, and the gas is collected in a graduated jar standing on the shelf of the pneumatic trough, the tube of the instrument, which is filled to the neck with dilute sulphuric acid, being passed beneath the jar.

Fig. 139.



The decompositions produced by the voltaic battery can be effected by the electricity of the common machine, by that developed by magnetic action, and by that of animal origin, but to an extent incomparably more minute. This arises from the very small quantity of electricity set in motion by the machine, although its *tension*—that is, power of overcoming obstacles, and passing through imperfect conductors—is exceedingly great. A pair of small wires of zinc and platinum, dipping into a single drop of dilute acid, develops far more electricity, to judge from the chemical effects of such an arrangement, than very many turns of a large plate electrical machine in powerful action. Nevertheless, polar or electrolytic decomposition can be distinctly and satisfactorily effected by the latter, although on a minute scale.

Theory of the Voltaic Battery.—With a knowledge of the principles just laid down, the study of the voltaic battery may be resumed and completed. In the first place, two very different views have been held concerning the source of the electrical disturbance in that apparatus. Volta himself ascribed it to mere contact of dissimilar metals or other substances conducting electricity,—to what was denominated an *electro-motive force*, called into being by such contact. Proof was supposed to be given of this fundamental proposition by an experiment in which disks of zinc and

copper attached to insulating handles, after being brought into close contact, were found, by the aid of a very delicate gold-leaf electroscope, to be in opposite electrical states. It appears, however, that the more carefully this experiment is made, the smaller is the effect observed; and hence it is judged highly probable that the whole may be due to accidental causes, against which it is almost impossible to guard.

On the other hand, the observation was soon made that the power of the battery always bears some kind of proportion to the chemical action upon the zinc; that, for instance, when pure water is used, the effect is extremely feeble; with a solution of salt, it becomes much greater; and, lastly, with dilute acid, greatest of all; so that some relation evidently exists between the chemical effect upon the metal and the evolution of electrical force.

The experiments of Faraday and Daniell have given very great support to the chemical theory, by showing that the contact of dissimilar metals is *not* necessary in order to call into being powerful electrical currents, and

Fig. 140.



that the development of electrical force is not only in some way connected with the chemical action of the liquid of the battery, but that it is always in direct proportion to the latter. One very beautiful experiment, in which electrolytic decomposition of potassium iodide is performed by a current generated without any contact of dissimilar metals, can be thus made: A plate of zinc is bent at a right angle, and cleaned by rubbing with sand-paper. A plate of platinum has a wire of the same metal attached to it by careful riveting, and the wire is bent into an arch. A piece of folded filter-paper is wetted with solution of potassium iodide, and placed upon the zinc; the platinum plate is arranged opposite to the latter, with the end of its wire resting upon the paper; and then the pair is plunged into a glass of dilute sulphuric, mixed with a few drops of nitric acid. A brown spot of iodine becomes in a moment evident beneath the extremity of the platinum wire—that is, at the positive side of the arrangement.

A strong argument in favor of the chemical view is founded on the easily proved fact that the direction of the current is determined by the kind of action upon the metals, the one least attacked being always positive. Let two polished plates, the one iron and the other copper, be connected by wires with a galvanometer, and then immersed in a solution of an alkaline sulphide. The needle in a moment indicates a powerful current, passing from the copper through the liquid to the iron, and back again through the wire. Let the plates be now removed, cleaned, and plunged into dilute acid; the needle is again driven round, but in the opposite direction, the current now passing from the iron through the liquid to the copper. In the first instance, the copper is acted upon, and not the iron; in the second, these conditions are reversed, and with them the direction of the current.

The metals employed in the construction of voltaic batteries are zinc for the active metal, and copper, silver, or, still better, platinum, for the inactive one: the greater the difference of oxidability, the better the arrangement. The liquid is either dilute sulphuric acid, sometimes mixed with a little nitric, or occasionally, where very slow and long-continued action is wanted, salt and water. To obtain the maximum effect of the apparatus with the least expenditure of zinc, that metal must be employed in a pure state, or its surface must be covered with an amalgam, which, in its electrical relations, closely resembles the pure metal. The zinc is easily brought into this condition by wetting it with dilute sulphuric acid, and then rubbing a little mercury over it, by means of a piece of rag tied to a stick.

The principle of the compound battery is, perhaps, best seen in the case of cups: by each alternation of zinc, fluid, and copper, the current is urged forwards with increased energy; its intensity is augmented, but the actual amount of electrical force thrown into the current form is not increased. The quantity, estimated by its decomposing power, is, in fact, determined by that of the smallest and least active pair of plates, the quantity of electricity in every part or section of the circuit being exactly equal. Hence, large and small plates, batteries strongly and weakly urged, can never be connected without great loss of power.

When a battery, either simple or compound, constructed with pure or even amalgamated zinc, is charged with dilute sulphuric acid, a number of highly interesting phenomena may be observed. While the circuit remains broken, the zinc is perfectly inactive, no acid is decomposed, no hydrogen liberated; but the moment the connection is completed, torrents of hydrogen arise, not from the zinc, but from the copper or platinum surfaces alone, while the zinc undergoes tranquil and imperceptible oxidation and solution. Thus, exactly the same effects are seen to occur in every active cell of a closed circuit, that are witnessed in a portion of sulphuric acid undergoing electrolysis: oxygen appears at the positive side, with respect to the current, and hydrogen at the negative; but with this difference that the oxygen, instead of being set free, combines with the zinc. It is, in fact, a real case of electrolysis, and electrolytes alone are available as exciting liquids.

Common zinc is very readily attacked and dissolved by dilute sulphuric acid, and this is usually supposed to arise from the formation of a multitude of little voltaic circles, by the aid of particles of foreign metals or impurities, partially imbedded in the zinc. This gives rise in the battery to what is called local action, by which, in the common forms of apparatus, three-fourths or more of the metal is often consumed, without contributing in the least to the general effect, but, on the contrary, injuring it to some extent. This evil is got rid of by amalgamating the surface.

By careful experiments, in which local action was completely avoided, it has been distinctly proved that the quantity of electricity set in motion by the battery varies exactly with the zinc dissolved. Coupling this fact with that of the definite action of the current, it will be seen that when a perfect battery of this kind is employed to decompose hydrochloric acid, in order to evolve 1 grain of hydrogen from the latter, 32.5 grains of zinc must be dissolved as chloride, and its equivalent quantity of hydrogen discharged in each active cell of the battery—that is to say, that the electrical force generated by the solution of an equivalent of zinc in the battery is capable of effecting the decomposition of an equivalent of hydrochloric acid or any other electrolyte out of it.

This is an exceedingly important discovery: it serves to show, in the most striking manner, the intimate nature of the connection between chemical and electrical forces, and their remarkable quantitative or equivalent relations. It almost seems, to use an expression of Faraday, as if a transfer of chemical force took place through the substance of solid metal-conductors; that chemical actions, called into play in one portion of the circuit, could be made at pleasure to exhibit their effects without loss or diminution in any other.

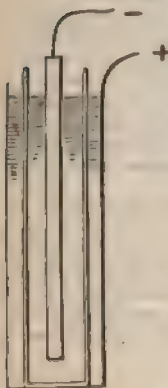
Electro-chemical Theory.—There is an hypothesis, not of recent date, long maintained and supported by the illustrious Berzelius, which refers all chemical phenomena to electrical forces—which supposes that bodies combine because they are in opposite electrical states; and that even the heat and light accompanying chemical union may be, to a certain extent, accounted for in this manner; that, in short, so far as our present knowledge

goes, either electric or chemical action may be assumed as cause or effect: it may be that electricity is merely a form or modification of ordinary chemical affinity; or, on the other hand, that all chemical action is a manifestation of electrical force.

This electro-chemical theory is no longer received as a true explanation of chemical phenomena to the full extent intended by its author. Berzelius, indeed, supposed that the combining tendencies of elements, and their functions in compounds, depend altogether on their electric polarity; and accordingly he divided the elements into two classes, the electro-positive, which, like hydrogen and the metals, move towards the negative pole of the battery, as if they were attracted by it, and the electro-negative, which, like oxygen, chlorine, and bromine, move towards the positive pole. We are, however, acquainted with a host of phenomena which show that the chemical functions of an element depend upon its position with regard to other elements in a compound, quite as much as upon its individual character. Thus chlorine, the very type of an electro-negative element, can be substituted for hydrogen, one of the most positive of the elements, in a large number of compounds, yielding new products, which exhibit the closest analogy in composition and properties to the compounds from which they are derived. It is impossible, therefore, to admit that the chemical functions of bodies are determined exclusively by their electrical relations. Still it is true in a general way that those elements which differ most strongly in their electrical characters, chlorine and potassium, for example, are likewise those which combine together with the greatest energy; and the division of bodies into electro-positive and electro-negative is therefore retained; the former are also called acid or chlorous, and the latter basylous or zincous.

Constant Batteries.—In all the older forms of the voltaic battery, such as those described on pages 110, 111, the power rapidly decreases, so that,

Fig 141.



after a short time, scarcely the tenth part of the original action remains. This loss of power depends, partly on the gradual change of the sulphuric acid into zinc sulphate, but still more on the coating of hydrogen, and, at a later stage, on the precipitation of metallic zinc on the copper plates. It is self-evident that if the copper plate in the liquid became covered with zinc, it would not electrically like a zinc plate.

An apparatus of immense value for purposes of electro-chemical research, in which it is desired to maintain powerful and equable currents for many successive hours, was contrived by the late Professor Daniell (fig. 141). Each cell of this "constant" battery consists of a copper cylinder $3\frac{1}{2}$ inches in diameter, and of a height varying from 6 to 18 inches. The zinc is employed in the form of a rod $\frac{3}{4}$ of an inch in diameter, carefully amalgamated, and suspended in the centre of the cylinder. A second cell of porous earthenware or animal membrane intervenes between the zinc and the copper: this is filled with a mixture of 1 part by measure of oil of vitriol and 8 of water, and the exterior space with the same liquid saturated with copper sulphate. A sort of little colander is fitted to

the top of the cell, in which crystals of the copper sulphate are placed, so that the strength of the solution may remain unimpaired. When a communication is made by a wire between the rod and the cylinder, a strong current is produced, the power of which may be increased to any extent by

connecting a sufficient number of such cells into a series, on the principle of the crown of cups, the copper of the first being attached to the zinc of the second. Ten such alternations constitute a very powerful apparatus, which has the great advantage of retaining its energy undiminished for a long time.

By this arrangement of the voltaic battery, the accumulation of hydrogen and deposition of zinc on the surface of the copper plate is altogether avoided, the zinc in the porous cell, whilst it dissolves in the sulphuric acid, decomposes it, but does not liberate any hydrogen; for by the progress of the decomposition, up to the boundary of the copper solution, the hydrogen takes the place of the copper, and thus ultimately the copper is precipitated on the copper plate. The copper plate therefore remains in its original state, so long as a sufficient quantity of copper sulphate is present in the solution.

By increasing the generative and reducing the antagonizing chemical affinities, Mr. Grove succeeded in forming the constant nitric acid battery which bears his name. This instrument is capable of producing a far greater degree of power than the battery previously mentioned, and hence it has become one of the most important means of promoting electrical science in the present day. The zinc dips into dilute sulphuric acid; and instead of a solution of copper, concentrated nitric acid is used, which surrounds a platinum plate. It is evident that the electrolytic action which begins at the zinc passes through the sulphuric acid, and in a precisely similar way through the contiguous nitric acid. Hydrogen would thus be liberated on the platinum plate. This action is not rendered visible by the evolution of gas, but only gradually by the change of color in the nitric acid: for the hydrogen liberated by the electrical action forms water at the expense of the oxygen yielded by the nitric acid; and by this means, so long as sufficient nitric acid is present, the purity of the surface of the platinum plate is maintained.

One of the cells in this battery is represented in section in fig. 142. The zinc plate is bent round, so as to present a double surface, and well amalgamated: within it stands a thin, flat cell of porous earthenware, filled with strong nitric acid, and the whole is immersed in a mixture of 1 part by measure of oil of vitriol and 6 of water, contained either in one of the cells of Wollaston's trough, or in a separate cell of glazed porcelain, made for the purpose. The apparatus is completed by a plate of platinum foil, which dips into the nitric acid, and forms the positive side of the arrangement. With ten such pairs, experiments of decomposition, ignition of wires, the light between charcoal points, &c., can be exhibited with great brilliancy, while the battery itself is very compact and portable, and, to a great extent, constant in its action. The zinc, as in the case of Daniell's battery, is consumed only while the current passes, so that the apparatus may be arranged an hour or two before it is required for use, which is also a matter of great convenience; and local action from the precipitation of copper on the zinc is avoided.

Professor Bunsen has modified the Grove battery by substituting for the platinum, dense charcoal or coke, which is an excellent conductor of electricity. By this alteration, at a very small expense, a battery may be made nearly as powerful and useful as that of Grove. On account of its cheapness, any one may put together one hundred or more of Bunsen's cells, by which the most magnificent phenomena of heat and light may be obtained.

142.

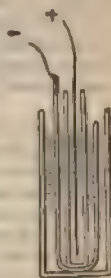


Figure 143 shows the form of the round carbon cylinder which is used in these cells. It is hollowed so as to receive a porous earthenware cell, in which a round plate of zinc is placed. The upper edge of the cylinder of carbon is well saturated with wax, and is surrounded by a copper ring, by means of which it may be put in connection with the zinc of the adjoining pair.

Fig. 143.



Bunsen's carbon cylinder is likewise well adapted for the use of dilute sulphuric acid alone, without the addition of nitric acid. It is, however, better to saturate the dilute sulphuric acid with potassium bichromate. When this mixture contains at least double the amount of sulphuric acid which is necessary to decompose the chromate, a battery is formed which surpasses in power the nitric acid battery, but does not furnish currents of the same constancy.

Mr. Smee has contrived an ingenious battery, in which silver, covered with a thin coating of finely divided metallic platinum, is employed in association with amalgamated zinc and dilute sulphuric acid. The rough surface appears to permit the ready disengagement of the bubbles of hydrogen.

Gas-battery.—Mr. Grove has contrived a battery in which an electrical current, of sufficient intensity to decompose dilute sulphuric acid, is produced by the action of oxygen upon hydrogen. Each element of this apparatus consists of a pair of glass tubes to contain the gases, dipping into a vessel of acidulated water. Both tubes contain platinum plates, covered with a rough deposit of finely divided platinum, and furnished with conducting wires, which pass through the tops or sides of the tubes, and are hermetically sealed into the latter. When the tubes are charged with oxygen on the one side and hydrogen on the other, and the wires connected with a galvanoscope, the needle of the instrument becomes instantly affected; and when ten or more are combined in a series, the oxygen tube of the one with the hydrogen-tube of the next, etc., while the terminal wires dip into acidulated water, a rapid stream of minute bubbles from either wire indicates the decomposition of the liquid; and when the experiment is made with a small voltmeter, it is found that the oxygen and hydrogen disengaged exactly equal in amount the quantities absorbed by the act of combination in each tube of the battery.

Electrotype.—Within the last forty years, several very beautiful and successful applications of voltaic electricity have been made, which may be slightly mentioned. Mr. Spencer and Professor Jacobi have employed it in copying, or rather in multiplying, engraved plates and medals, by depositing upon their surfaces a thin coating of metallic copper, which, when separated from the original, exhibits, in reverse, a most faithful representation of the latter. By using this in its turn as a mould or matrix, an absolutely perfect *fac-simile* of the plate or medal is obtained. In the former case, the impressions taken on paper are quite undistinguishable from those directly derived from the work of the artist; and as there is no limit to the number of *electrotype* plates which can be thus produced, engravings of the most beautiful description may be multiplied indefinitely. The copper is very tough, and bears the action of the press perfectly well.

The apparatus used in this and many similar processes is of the simplest kind. A trough or cell of wood is divided by a porous diaphragm, made of a very thin piece of sycamore, into two parts; dilute sulphuric acid is

put on one side, and a saturated solution of copper sulphate, sometimes mixed with a little acid, on the other. A plate of zinc is soldered to a wire or strip of copper, the other end of which is secured by similar means to the engraved copper plate. The latter is then immersed in the solution of sulphate, and the zinc in the acid. To prevent deposition of copper on the back of the copper plate, that portion is covered with varnish. For medals and small works, a porous earthenware cell, placed in a jelly-jar, may be used.

Fig. 144.



Other metals may be precipitated in the same manner, in a smooth and compact form, by the use of certain precautions which have been gathered by experience. Electro-gilding and plating are now carried on very largely and in great perfection by Messrs. Elkington and others. Even non-conducting bodies, as sealing-wax and plaster of Paris, may be coated with metal; it is only necessary, as shown by the late Mr. Robert Murray, to rub over them the thinnest possible film of plumbago. Seals may thus be coated in a very few hours with unerring truth.

The common but very pleasing experiment of the *lead-tree* is greatly dependent on electro-chemical action. When a piece of zinc is suspended in a solution of lead acetate, the first effect is the decomposition of a portion of the latter, and the deposition of metallic lead upon the surface of the zinc; it is simply a displacement of a metal by a more oxidable one. The change does not, however, stop here; metallic lead is still deposited in large and beautiful plates upon that first thrown down, and the solution becomes exhausted, or the zinc entirely disappears. The first portions of the lead form with the zinc a voltaic arrangement of sufficient power to decompose the salt: under the peculiar circumstances in which the zinc is placed, the metal is precipitated upon the negative portion—that is, the lead—while the oxygen and acid are taken up by the zinc.

Fig. 145.



Bequerel, several years ago, published an exceedingly interesting account of certain experiments in which crystallized metals, oxides, and other insoluble substances had been produced by the slow and continuous action of feeble electrical currents, kept up for months, or even years. These products exactly resemble natural minerals: and, indeed, the experiments throw great light on the formation of the latter within the earth.*

Heat developed by the Electric Current.—All parts of the electric circuit, the plates, the liquid in the cells of the battery, the conducting wires, and the electrolytes undergoing decomposition, all become heated during the passage of the current. The rise of temperature in any part of the circuit depends partly on the strength of the current, partly on its resistance, those bodies which offer the greatest resistance, or are the worst conductors, being most strongly heated by a current of given strength. Thus, when a thick and a thin wire of the same metal are included in the same circuit, the latter becomes most strongly heated, and a platinum wire is much more strongly heated than a silver or copper wire of the same thickness.

By exact experiments it has been found that both in metallic wires and in liquids traversed by an electric current, the evolution of heat is directly proportional—1st, to the resistance; 2d, to the strength of the current. Joule has also shown that the evolution of heat in each couple of the voltaic

* *Traité de l'Electricité et du Magnétisme*, III. 230.
† *Phil. Mag.* [2] xix. 20.

battery is subject to the same law, which, therefore, holds good in every part of the circuit, including the battery.

The strength of an electric current is measured by the quantity of detonating gas (2 vols. H to 1 vol. O) which it can evolve from acidulated water in a given time, and the unit of current strength is the current which eliminates one cubic centimetre of detonating gas at 0° C. and 760^{mm} barometric pressure in a minute. Now Lenz has shown that when a current of the unit of strength passes through a wire whose resistance is equal to that of a copper wire 1 metre long and 1 millimetre in diameter, it develops a quantity of heat sufficient to raise the temperature of 1 gram of water from 0° to 1° C. in $5\frac{1}{2}$ minutes; and assuming as the unit of heat the quantity required to raise the temperature of 1 gram of water from 0° to 1° C., the law may be thus expressed—

A current of the unit of strength passing through a conductor which exerts the unit of resistance, develops therein 1.057 heat-unit in an hour, or 0.0176 heat-unit in a minute.

With a current of given strength, the sum of the quantities of heat evolved in the battery and in the metallic conductor joining its poles, is constant, the heat actually developed in the one part or the other varying according to the thickness of the metallic conductor. This was first shown by De la Rive, and has been confirmed by Favre.* De la Rive made use of a couple consisting of platinum and distilled zinc or cadmium, excited by pure and very strong nitric acid, the two metals being united by a platinum wire, more or less thick, which was plunged into the same quantity of strong nitric acid contained in a capsule, similar to that which held the voltaic couple. By observing the temperatures in the two vessels with delicate thermometers, the sum of these temperatures was found to be constant, the one or the other being greater according to the thickness of the connecting wire.

Favre,† by means of a calorimeter, similar to that which he used in his experiments on the development of heat by chemical action, has shown that in a pair of zinc and platinum plates, excited by dilute sulphuric acid and connected by platinum wires of various length and thickness, for every 32.5 grams of zinc dissolved, a quantity of heat is developed in the entire circuit equal to 18,173 heat-units, but variously distributed between the battery-cell and the wire, according to the thickness of the latter. Now, this quantity of heat is nearly the same as that which is evolved in the simple solution of 32.5 grams of zinc in dilute sulphuric acid, without the formation of a voltaic circuit, viz., 18,444 units. Hence, Favre concludes that the heat developed by the resistance of a metallic or other conductor connecting the poles of the battery is simply borrowed from the total quantity of heat evolved by the chemical action taking place in the battery, and is rigorously complementary to that which remains in the cells of the battery, the heat evolved in the entire circuit being the exact equivalent of the chemical action which takes place. If any external work is performed by the current, such as electrolysis, or mechanical work, as by an electro-magnetic engine, the heat evolved in the circuit is diminished by the heat-equivalent of the decomposition or mechanical work done.

* Ann. Ch. Phys. [3] xl. 393.

† Comptes Rendus, xlv. 86.

CHEMISTRY OF THE METALS.

The metals constitute the second and larger group of elementary bodies. A great number of them are of very rare occurrence, being found only in a few scarce minerals; others are more abundant, and some few almost universally diffused throughout the globe. Some of these bodies are of most importance when in the metallic state; others, when in combination, chiefly as oxides, the metals themselves being almost unknown. Many are used in medicine and in the arts, and are essentially connected with the progress of civilization.

If arsenic be included, the metals amount to fifty in number.

Physical Properties.—One of the most remarkable and striking characters possessed by the metals is their peculiar lustre: this is so characteristic that the expression *metallic lustre* has passed into common speech. This property is no doubt connected with the great degree of opacity which the metals present in every instance. The thinnest leaves or plates, and the edges of crystalline laminae, arrest the passage of light in the most complete manner. An exception to the rule is usually made in favor of gold-leaf, which, when held up to the daylight, exhibits a greenish, and, in some cases, a purple color, as if it were really endued with a certain degree of translucency: the metallic film is, however, generally so imperfect that it is somewhat difficult to say whether the observed effect may not be in some measure due to multitudes of little holes, many of which are visible to the naked eye; but Faraday's experiments have established the translucency of gold beyond all doubt.

In point of color, the metals present a certain degree of uniformity: with two exceptions—viz., copper, which is red, and gold, which is yellow—all these bodies are included between the pure white of silver and the bluish-gray tint of lead: bismuth, it is true, has a pinkish color, and calcium and strontium, a yellowish tint, but these tints are very feeble.

The differences of *specific gravity* are very wide, passing from lithium, potassium, and sodium, which are lighter than water, to platinum, which is more than twenty-one times heavier than an equal bulk of that liquid.

Table of the Specific Gravities of Metals at 15.5° C. (60° F.).

| | |
|-------------------------|---------------|
| Platinum (in thin wire) | 21.50 |
| Gold | 19.50 |
| Titanium | 18.40 |
| Tungsten | 17.60 |
| Mercury | 13.59 |
| Palladium | 11.30 to 11.8 |
| Lead | 11.45 |
| Silver | 10.50 |
| Bismuth | 9.90 |
| Copper | 8.96 |
| Nickel | 8.80 |
| Cadmium | 8.70 |
| Molybdenum | 8.63 |
| Cobalt | 8.54 |
| Manganese | 8.00 |

| | |
|---------------------|--------------|
| Iron | 7.79 |
| Tin | 7.29 |
| Zinc | 6.86 to 7.1 |
| Antimony | 6.80 |
| Arsenic | 5.88 |
| Aluminium | 2.56 to 2.67 |
| Magnesium | 1.75 |
| Sodium | 0.972 |
| Potassium | 0.865 |
| Lithium | 0.593 |

The property of *malleability*, or power of extension under the hammer, or between the rollers of the flattening-mill, is possessed by certain of the metals to a very great extent. Gold-leaf is a remarkable example of the tenuity to which a malleable metal may be brought by suitable means. The gilding on silver wire used in the manufacture of gold lace is even thinner, and yet presents an unbroken surface. Silver may be beaten out very thin—copper also, but to an inferior extent; tin and platinum are easily rolled out into foil; iron, palladium, lead, nickel, cadmium, the metals of the alkalis, and mercury when solidified, are also malleable. Zinc may be placed midway between the malleable and brittle division; then perhaps bismuth; and, lastly, such metals as antimony and arsenic, which are altogether destitute of malleability.

The specific gravity of malleable metals is usually very sensibly increased by pressure or blows, and the metals themselves are rendered much harder, with a tendency to brittleness. This condition is destroyed and the former soft state restored by the operation of *annealing*, which consists in heating the metal to redness out of contact with air (if it will bear that temperature without fusion), and cooling it, quickly or slowly according

to the circumstances of the case. After this operation, it is found to possess its original specific gravity.

Fig. 146.



Ductility is a property distinct from the last, inasmuch as it involves the principle of tenacity, or power of resisting tension. The art of wire-drawing is one of great antiquity; it consists in drawing rods of metal through a succession of trumpet-shaped holes in a steel plate, each being a little smaller than its predecessor, until the requisite degree of fineness is attained. The metal often becomes very hard and rigid in this process, and is then liable to break; this is remedied by annealing. The order of tenacity among the metals susceptible of being

easily drawn into wire is the following: it is determined by observing the weights required to break assunder wires drawn through the same orifice of the plate:—

| | |
|-----------|-------|
| Iron. | Gold. |
| Copper. | Zinc. |
| Platinum. | Tin. |
| Silver. | Lead. |

Metals differ as much in *fusibility* as in density. The following table will give an idea of their relations to heat:—

| | | Melting Points. | |
|--------------------------------|---|--|----------|
| | | F. | C. |
| Fusible below
a red heat. | Mercury | — 39° | — 39.44° |
| | Rubidium | + 101.3 | + 38.5 |
| | Potassium | 144.5 | 62.5 |
| | Sodium | 207.7 | 97.6 |
| | Lithium | 356 | 180 |
| | Tin | 442 | 227.8 |
| | Calcium (about) | 442 | 228 |
| | Bismuth | 497 | 258 |
| | Thallium | 561 | 294 |
| | Lead | 617 | 325 |
| | Tellurium—rather less fusible than lead | | |
| | Arsenic—unknown | | |
| | Zinc | 773 | 412 |
| Infusible below
a red heat. | Antimony—just below redness | | |
| | Silver | 1873 | 1023 |
| | Copper | 1906 | 1091 |
| | Gold | 2016 | 1142 |
| | Cast-iron | 2786 | 1530 |
| | Pure iron | Highest heat of Forge. | |
| | Nickel | | |
| | Cobalt | | |
| | Manganese | | |
| | Palladium | Agglomerate, but do not melt in the forge. | |
| | Molybdenum, | | |
| | Uranium, | | |
| | Tungsten, | | |
| | Chromium, | Infusible in ordinary blast-furnaces ;
fusible by oxy-hydrogen blow-pipe. | |
| | Titanium, | | |
| | Cerium, | | |
| | Osmium, | | |
| | Iridium, | | |
| | Rhodium, | | |
| | Platinum, | | |
| | Tantalum, | | |

Some metals acquire a pasty or adhesive state before becoming fluid : this is the case with iron and platinum, and with the metals of the alkalies. It is this peculiarity which confers the very valuable property of welding, by which pieces of iron and steel are united without solder, and the finely divided metallic sponge of platinum is converted into a solid and compact bar.

Some metals are *volatile*, and this character would perhaps be exhibited by all, could temperatures sufficiently elevated be obtained. Mercury boils and distils below a red heat : potassium, sodium, zinc, magnesium, and calcium rise in vapor when heated to bright redness ; arsenic and tellurium are volatile.

CHEMICAL RELATIONS OF THE METALS.

METALLIC combinations are of two kinds—namely, those formed by the union of metals among themselves, which are called alloys, or where mercury is concerned, *amalgams*, and those generated by combination with

the non-metallic elements, as oxides, chlorides, sulphides, etc. In this latter case, the metallic characters are almost invariably lost.

Alloys.—Most metals are probably, to some extent, capable of existing in a state of combination with each other in definite proportions; but it is difficult to obtain these compounds in a separate state, since they dissolve in all proportions in the melted metals, and do not generally differ so widely in their melting points from the metals they may be mixed with, as to be separated by crystallization in a definite form. Exceptions to this rule are met with in the cooling of argentiferous lead, and in the crystallization of brass and of gun-metal.

The chemical force capable of being exerted between different metals is for the most part very feeble, and the consequent state of combination is therefore very easily disturbed by the influence of other forces. The stability of such metallic compounds is, however, greater in proportion to the general dissimilarity of the metals they contain. But in all cases of combination between metals, the alteration of physical characters, which is the distinctive feature of chemical combination, does not take place to any great extent. The most unquestionable compounds of metals with metals are still metallic in their general physical characters, and there is no such transmutation of the individuality of their constituents as takes place in the combination of a metal with oxygen, sulphur, chlorine, etc. The alteration of characters in alloys is generally limited to the color, degree of hardness, tenacity, etc., and it is only when the constituent metals are capable of assuming opposite chemical relations that these compounds are distinguished by great brittleness.

The formation of actual chemical compounds, in some cases, when two metals are melted together, is indicated by several phenomena, viz., the evolution of heat, as in the case of platinum and tin, copper and zinc, etc. The density of alloys differs from that of mere mixtures of the metals. In the solidification of alloys, the temperature does not always fall uniformly, but often remains stationary at particular degrees, which may be regarded as the solidifying points of the compounds then crystallizing. Tin and lead melted together in any proportions always form a compound which solidifies at 187° . The melting point of an alloy is often very different from the point of solidification, and it is generally lower than the mean melting point of the constituent metals.

But though metals may combine when melted together, it is doubtful whether they remain combined after the solidification of the mass, and the wide differences between the melting and solidifying points of certain alloys appear to indicate that the existence of these compounds is limited to a certain range of temperature. Matthiessen* regards it as probable that the condition of an alloy of two metals in the liquid state may be either that of—1. A solution of one metal in another; 2. Chemical combination; 3. Mechanical mixture; or, 4. A solution or mixture of two or all of the above; and that similar differences may exist as to its condition in the solid state.

The chemical action of reagents upon alloys is sometimes very different from their action upon metals in the separate state: thus, platinum alloyed with silver is readily dissolved by nitric acid, but is not affected by that acid when unalloyed. On the contrary, silver, which in the separate state is readily dissolved by nitric acid, is not dissolved by it when alloyed with gold in proportions much less than one-fourth of the alloy by weight.

* British Association Reports, '563, p. 97.

Compounds of Metals with Metalloids.—Classification of Metals.

A classification of the metals according to their quantivalence or atomity is given in the table on p. 239; and each of the classes thus formed may be divided into groups, the individual members of which possess certain physical or chemical characters in common. There are, however, several metals, especially among those of rare occurrence, whose position in the series is by no means definitely fixed.

CLASS I.—Monad Metals.—1. Among these metals, potassium, sodium, cesium, rubidium, and lithium are called *alkali-metals*. They are soft, easily fusible, volatile at higher temperatures; combine very energetically with oxygen; decompose water at all temperatures; and form strongly basic oxides, which are very soluble in water, yielding powerfully caustic and alkaline hydroxides, not decomposable by heat. Their carbonates are soluble in water, and each metal forms only one chloride. The hypothetical metal ammonium, NH_4 (p. 158), is usually added to the list of alkali-metals, on account of the general similarity of its compounds to those of potassium and sodium.

2. Silver differs greatly from the alkali-metals in its physical and most of its chemical properties, but it is related to them by the isomorphism of some of its compounds with the corresponding compounds of these metals; thus it forms an alum, similar in form and composition to ordinary potash alum.

CLASS II.—Dyad Metals.—1. The three metals, barium, strontium, and calcium, form oxides called *alkaline earths*, less soluble in water than the true alkalis, but exhibiting similar taste, causticity, and action on vegetable colors. The metals of this group form but one chloride, e.g., BaCl_2 ; their carbonates are insoluble in water, and barium sulphate is also insoluble, strontium and calcium sulphates slightly soluble.

2. A second group consists of the metals beryllium, yttrium, erbium, lanthanum, and didymium, which form oxides called *earths*, insoluble in water, and not reducible to the metallic state by hydrogen or carbon; their carbonates are insoluble in water, their sulphates soluble. These metals also form but one chloride, viz., a dichloride. They are all very rare. Mendelejeff, as already observed (p. 239), proposes to classify didymium, yttrium, and erbium as triads, and lanthanum as a tetrad; but his reasons for doing so are not very conclusive: at all events it is most convenient to describe these metals amongst the earth-metals.

3. Magnesium, zinc, and cadmium resemble one another in being volatile at high temperatures, and burning when heated in the air: they decompose water at high temperatures, eliminate hydrogen from dilute acids, and form only one oxide and one chloride, e.g., ZnO and ZnCl_2 . Magnesium was formerly classed as an earth-metal, but it bears a much nearer analogy to zinc.

4. Mercury and copper each form two chlorides and two oxides: mercury, for example, forms the two chlorides, HgCl_2 and Hg_2Cl_2 , and the two oxides, HgO and Hg_2O . Mercurous chloride (calomel) is represented

by the formula $\begin{array}{c} \text{Hg}-\text{Cl} \\ | \\ \text{Hg}-\text{Cl} \end{array}$, and the corresponding oxide by $\begin{array}{c} \text{Hg} \\ | \\ \text{Hg} > \text{O} \end{array}$

The copper compounds are similarly constituted. These metals do not decompose water at any temperature; they are oxidized by nitric and by

strong sulphuric acids. The oxides of mercury are reduced to the metallic state by heat alone; those of copper by ignition with hydrogen or charcoal.

The position of copper in the series has already been discussed (p. 239). It has certain analogies with the metals of the iron group—and in the cuprous compounds it may be regarded as univalent; but in its most stable compounds, the cupric salts, it is unquestionably bivalent.

CLASS III.—Triad Metals.—The metals referable to this class are aluminium, gallium, indium, thallium, and gold. The first three form only trichlorides; thallium and gold form monochlorides and trichlorides, also corresponding oxides, *e. g.*, thallium chlorides, TlCl and TlCl_3 ; oxides, Tl_2O and Tl_2O_3 . The mono-compounds of thallium are much more stable than the tri-compounds, and in respect of these compounds thallium exhibits very close analogies to the alkali-metals, forming, for example, an alum isomorphous with common potash alum, and phosphates analogous in composition to the phosphates of sodium. The position of gold has already been discussed. Aluminium is sometimes regarded as a tetrad, but for reasons already given (p. 240) it is most probably a triad.

CLASS IV.—Tetrad Metals.—To this class belong zirconium, thorium, cerium, tin, titanium, and lead. Zirconium and thorium form tetrachlorides and dioxides. The position of cerium in the series is altogether doubtful.

Tin and titanium are closely related to silicon, each forming a volatile tetrachloride; namely, stannic chloride, SnCl_4 , and titanous chloride, TiCl_4 , together with the corresponding oxides. Tin likewise forms the stannous compounds in which it is bivalent, *e. g.*, SnCl_2 , SnO ; and titanium forms the titanous compounds, in which it is apparently trivalent, but really quadrivalent: *e. g.*, TiCl_3 or $\text{Ti}_2\text{Cl}_6 = \text{Cl}_2\text{Ti} - \text{TiCl}_3$.

The quadrivalence of lead is inferred from the composition of *plumbo-tetrachloride*, $\text{Pb}(\text{Cl}_2)_4$; but in most of its compounds it is bivalent, forming only one chloride, PbCl_2 , with corresponding iodide, bromide, and fluoride. It forms also the corresponding oxide, PbO , together with a lower oxide, Pb_2O_3 , and three higher oxides, Pb_3O_4 , Pb_4O_6 , and PbO_2 . Lead is allied to barium and strontium by the isomorphism of its sulphate with the sulphates of barium and strontium, and to silver, thallium, and mercury by the sparing solubility of its chloride, which is precipitated by hydrochloric acid from solutions of lead salts.

Platinum and its allied metals also form tetrachlorides and dioxides; but these metals are best regarded as forming a group by themselves.

CLASS V.—Pentad Metals.—1. Arsenic forms a trichloride, a trioxide, and corresponding salts, also a pentoxide, and corresponding salts, called arsenates, analogous to the phosphates. Antimony forms a trichloride and a pentachloride analogous to those of phosphorus, also the corresponding oxides. Bismuth forms a volatile trichloride, and a di-

chloride, Bi_2Cl_6 or $\begin{array}{c} \text{BiCl}_3 \\ | \\ \text{BiCl}_3 \end{array}$. Vanadium was formerly supposed to belong

to the tungsten group, but it has lately been shown to be a pentad. It forms a trichloride, VCl_3 ; also an oxychloride, VOCl_3 , analogous to phosphorus oxychloride, and the oxides, V_2O_3 and V_2O_5 , analogous to those of phosphorus and arsenic, the latter yielding a series of salts, the vanadates, isomorphous with the phosphates and arsenates of corresponding composition.

2. *Tantalum* and *niobium*, formerly regarded as tetrads, have been

down by Marignac to form pentachlorides and pentoxides. The oxides of the pentad metals are, for the most part, of acid character.

Class VI.—Hexad Metals.—1. Chromium forms a hexfluoride, CrF_6 , and a corresponding oxide, CrO_3 . It likewise forms two series of compounds, in which it exhibits lower degrees of equivalence, viz., the chromic compounds analogous to the ferric compounds, in which, like aluminium and iron, it is either trivalent or quadrivalent; e. g., chromic chloride,

CrCl_3 or $\text{Cr}_2\text{Cl}_6 = \begin{array}{c} \text{CrCl}_3 \\ | \\ \text{CrCl}_3 \end{array}$; and the chromous compounds, analogous to the ferrous compounds, in which it is bivalent, e. g., CrCl_2 , CrO .

Uranium forms a trioxide, UO_3 , and an oxychloride, UO_2Cl_2 , analogous to CrO_3 and CrCl_3 .

2. Tungsten forms a hexchloride, WCl_6 , and the corresponding oxide, WO_3 . Molybdenum is not known to form a chloride higher than MoCl_5 , but its trioxide, MoO_3 , is known; and, from the general similarity of the tungsten and molybdenum compounds, the latter metal is inferred to be tetradic.

Class VII.—Heptad Metals.—The only metal at present referable to this class is Manganese, which forms a heptachloride, and may also be regarded as heptadic in permanganic acid, HMnO_4 , and its salts, which, as already observed, are isomorphous with the perchlorates (p. 241). Manganese is, however, more conveniently described in connection with the one group of metals.

Class VIII.—Iron and Platinum Metals.—These metals, for reasons already mentioned, cannot be referred to either of the preceding classes (p. 241). Besides possessing certain physical properties in common, they exhibit a greater tendency than any of the preceding to enter into combination, sometimes as perissads, sometimes as artiads.

The nine metals of this class resemble one another in many respects; (1) They are all of gray color and difficult of fusion. (2) They possess to a high degree the power of condensing and giving passage to gases, as seen especially in nickel, palladium, iron, and platinum. (3) Their highest oxides are bases, or acids of little energy, which are easily reduced to lower oxides of more decided basic character. (4) They form stable soluble cyanides with the alkali-metals, Fe, Ru, and Os, yielding analogous compounds having the general formula K_2RCy_6 ; Co, Rh, Ir, forming salts having the general formula K_2RCy_6 ; Ni, Pd, Pt, forming salts having the composition K_2RCy_4 . (5) Some of their compounds, especially those of the higher degrees of combination, are distinguished by characteristic colors.

Copper and gold might, on account of analogous behavior, be included in the eighth class, although, according to the constitution of their lower oxides, they belong to the first or monadic class.

The *Iron Group* includes iron, nickel, and cobalt, perhaps also manganese, chromium, and cerium. Iron, in the ferrous compounds, is bivalent; in the ferric compounds, it may be regarded either as trivalent or as quadrivalent, ferric chloride, for example, being either FeCl_3 or $\text{Fe}_2\text{Cl}_6 = \begin{array}{c} \text{Cl}_3\text{Fe} \\ | \\ \text{FeCl}_3 \end{array}$. The vapor-density of the compound tends rather to support the latter formula. Iron also forms salts called ferrates, analogous to the chromates, in which it is hexvalent. Cobalt forms two series of compounds analogous to the ferrous and ferric compounds; nickel is, for the most part, bivalent, but it also forms a sesquioxide, Ni_3O_4 .

Manganese, as above mentioned, is septivalent in its highest chloride, $MnCl_7$ (the composition of which is, however, somewhat doubtful), and in the permanganates; in its other compounds it resembles iron, being bivalent in the manganous, tri- or quadrivalent in the manganic compounds, and sexvalent in the manganates, *e. g.*, K_2MnO_4 , which are analogous to the sulphates, chromates, and ferrates. All these metals decompose water at high temperatures. Nickel and cobalt are magnetic like iron, and their salts are isomorphous with the corresponding iron compounds.

Chromium forms three series of compounds analogous in composition and in many of their properties to the ferrous and ferric salts and the ferrates. Chromic acid, however, and the corresponding anhydride are very stable compounds; whereas, ferric acid and the corresponding anhydrous oxide, FeO_3 , are unknown, and the ferrates are very unstable. Cerium, is bivalent in the cerous salts, sexvalent in ceric fluoride, CeF_6 , and forms an oxide, Ce_2O_3 , analogous to ferroso-ferric oxide, Fe_2O_3 , and corresponding salts.

Platinum Metals.—Platinum, palladium, iridium, rhodium, ruthenium, and osmium, form a natural group of metals, occurring together in the metallic state, and resembling each other in many of their properties. Platinum and palladium form dichlorides and tetrachlorides, with corresponding oxides, *viz.*, $PtCl_2$, $PtCl_4$, PtO , PtO_2 . Iridium forms a dichloride, a tetrachloride, and an intermediate chloride, which may be regarded either as $IrCl_3$ or as $Ir_2Cl_6 = Cl_3Ir-IrCl_3$. Ruthenium and osmium form chlorides similar in constitution to those of iridium; rhodium only a dichloride, $RhCl_2$, and a trichloride, Rh_2Cl_6 . All these metals form oxides analogous in composition to their chlorides, *e. g.*, IrO , Ir_2O_3 , IrO_2 , and likewise higher oxides, iridium and rhodium forming tri-oxides, IrO_3 and RhO_3 , and osmium and ruthenium forming tetroxides, OsO_4 and RuO_4 ; but there are no chlorides corresponding with these oxides. The metals of the platinum group are not acted upon by nitric acid, but only by chlorine or nitro-muriatic acid. With the exception of osmium, they do not oxidize in the air at any temperature, and their oxides are all reducible by heat alone. These metals, together with gold, silver, and mercury, which likewise exhibit the last-mentioned character, are sometimes called *noble metals*.

The metals of the alkalis and alkaline earths, on account of their inferior specific gravity, are often called *light metals*; the others, *heavy metals*.

Metallic Chlorides.—All metals combine with chlorine, and most of them in several proportions, as above indicated, forming compounds which may be regarded as derived from one or more molecules of hydrochloric acid, by substitution of a metal for an equivalent quantity of hydrogen; thus:—

| | | | | |
|-------------|-------------|----------------|------|----------------------|
| From HCl | are derived | monochlorides | like | KCl |
| " H_2Cl_2 | " | dichlorides | " | $BaCl_2$ |
| " H_3Cl_3 | " | trichlorides | " | $AuCl_3$ |
| " H_4Cl_4 | " | tetrachlorides | " | $SuCl_4$, etc. etc. |

Hydrochloric acid may, in fact, be regarded as the type of chlorides in general.

Several chlorides occur as natural products. Sodium chloride, or *common salt*, occurs in enormous quantities, both in the solid state as rock-

salt, and dissolved in sea-water, and in the water of rivers and springs. Potassium chloride occurs in the same forms, but in smaller quantity; the chlorides of lithium, cesium, rubidium, and thallium also occur in small quantities in certain spring waters. Mercurous chloride, Hg_2Cl_2 , and silver chloride, AgCl , occur as natural minerals.

1. Chlorides are generally prepared by one or other of the following processes: (1) By acting upon the metal with chlorine gas. Antimony pentachloride and copper dichloride are examples of chlorides sometimes produced in this manner. The chlorides of gold and platinum are usually prepared by acting upon the metals with nascent chlorine, developed by hydrochloric and nitric acids. Sometimes, on the other hand, the metal is in the nascent state, as when titanous chloride is formed by passing a current of chlorine over a heated mixture of charcoal and titanous oxide. The chlorides of aluminium and chromium may be obtained by similar processes.

2. Chlorine gas, by its action upon metallic oxides, drives out the oxygen, and unites with the respective metals to form chlorides. This reaction sometimes takes place at ordinary temperatures, as in the case with silver oxide; sometimes only at a red heat, as is the case with the oxides of the alkali-metals, and alkaline earth-metals. The hydroxides and carbonates of these last metals, when dissolved or suspended in hot water and treated with excess of chlorine, are converted, chiefly into chlorides, partly into chlorates.

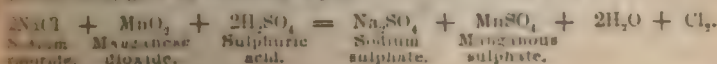
3. Many metallic chlorides are prepared by acting upon the metals with hydrochloric acid. Zinc, cadmium, iron, nickel, cobalt, and tin dissolve readily in hydrochloric acid, with liberation of hydrogen; copper only in the strong boiling acid; silver, mercury, palladium, platinum, and gold, not at all. Sometimes the metal is substituted, not for hydrogen, but for another metal. Stannous chloride, for instance, is frequently made by adding metallic tin with mercurous chloride; thus: $\text{Hg}_2\text{Cl}_2 + \text{Sn} = \text{SnCl}_2 + \text{Hg}$.

4. By dissolving a metallic oxide, hydroxide, or carbonate in hydrochloric acid.

All monochlorides and dichlorides are soluble in water, excepting silver chloride, AgCl , and mercurous chloride, Hg_2Cl_2 ; lead chloride, PbCl_2 , is sparingly soluble; these three chlorides are easily formed by precipitation. Many metallic chlorides dissolve also in alcohol and in ether.

Most monochlorides, dichlorides, and trichlorides volatilize at high temperatures without decomposition; the higher chlorides when heated give off part of their chlorine. Some chlorides which resist the action of heat are decomposed by ignition in the air, yielding metallic oxides and free chlorine: this is the case with the dichlorides of iron and manganese; but most dichlorides remain undecomposed, even in this case. All metal-trichlorides, excepting those of the alkali-metals and earth-metals, are decomposed at a red heat by hydrogen gas, with formation of hydrochloric acid: in this way metallic iron may be obtained in fine cubical crystals. Silver chloride, placed in contact with metallic zinc or iron, under dilute sulphuric or hydrochloric acid, is reduced to the metallic state by the nascent hydrogen.

Sulphuric, phosphoric, boric, and arsenic acids decompose most metallic chlorides, sometimes at ordinary, sometimes at higher temperatures. All metallic chlorides, heated with lead dioxide or manganese dioxide and sulphuric acid, give off chlorine, e. g.:



Chlorides distilled with sulphuric acid and potassium chromate, yield a dark bluish-red distillate of chromic oxychloride. Some metallic chlorides are decomposed by water, forming hydrochloric acid and an oxychloride, e. g.: $\text{BiCl}_3 + \text{H}_2\text{O} = 2\text{HCl} + \text{BiClO}$. The chlorides of antimony and stannous chloride are decomposed in a similar manner.

All soluble chlorides give, with solution of *silver nitrate*, a white precipitate of silver chloride, easily soluble in ammonia, insoluble in nitric acid. With *mercurous nitrate*, they yield a white curdy precipitate of mercurous chloride, blackened by ammonia; and with *lead-salts*, not too dilute, a white precipitate of lead chloride, soluble in excess of water.

Metallic chlorides unite with each other and with the chlorides of the non-metallic elements, forming such compounds as potassium chloromercurate, 2KCl.HgCl_2 , sodium chloroplatinate, 2NaCl.PtCl_4 , potassium chloriodate, KCl.ICl_3 , etc. Metallic chlorides combine in definite proportions with ammonia and organic bases: the chlorides of platinum form with ammonia the compounds $2\text{NH}_3.\text{PtCl}_2$, $4\text{NH}_3.\text{PtCl}_2$, $2\text{NH}_3.\text{PtCl}_4$, and $4\text{NH}_3.\text{PtCl}_4$; mercuric chloride forms with aniline the compound $2\text{C}_6\text{H}_5\text{N.HgCl}_2$, etc.

Chlorides also unite with oxides and sulphides, forming *oxychlorides* and *sulphochlorides*, which may be regarded as chlorides having part of their chlorine replaced by an equivalent quantity of oxygen or sulphur (Cl_2 by O or S). Bismuth, for example, forms an oxychloride having the composition BiClO or $\text{BiCl}_2.\text{Bi}_2\text{O}_3$.

Bromides.—Bromine unites directly with most metals, forming compounds analogous in composition to the chlorides, and resembling them in most of their properties. The bromides of the alkali-metals occur in seawater and in many saline springs; silver bromide occurs as a natural mineral. Nearly all bromides are soluble in water, and may be formed by treating an oxide, hydroxide, or carbonate, with hydrobromic acid, the solutions when evaporated giving off water for the most part, and leaving a solid metallic bromide; some of them, however, namely, the bromides of magnesium, aluminium, and the other earth-metals, are more or less decomposed by evaporation, giving off hydrobromic acid, and leaving a mixture of metallic bromide and oxide. Silver bromide and mercurous bromide are insoluble in water, and lead bromide is very sparingly soluble; these are obtained by precipitation.

Metallic bromides are solid at ordinary temperatures; most of them fuse at a moderate heat, and volatilize at higher temperatures. The bromides of gold and platinum are decomposed by mere exposure to heat; many others give up their bromine when heated in contact with the air. Chlorine, with the aid of heat, drives out the bromine and converts them into chlorides. Hydrochloric acid also decomposes them at a red heat, giving off hydrobromic acid. Strong sulphuric or nitric acid decomposes them, with evolution of hydrobromic acid, which, if the sulphuric or nitric acid is concentrated, and in excess, is partly decomposed, with separation of bromine and formation of sulphurous oxide or nitrogen dioxide. Bromides heated with sulphuric acid and manganese dioxide or potassium chromate, give off free bromine.

Bromides in solution are easily decomposed by chlorine, either in the form of gas or dissolved in water, the liquid acquiring a red or reddish-yellow color, according to the quantity of bromine present; and on agitating the liquid with ether, that liquid dissolves the bromine, forming a red solution, which rises to the surface.

Soluble bromides give with *silver nitrate* a white precipitate of silver bromide, greatly resembling the chloride, but much less soluble in ammonia, insoluble in hot nitric acid. Mercurous nitrate produces a yellowish-

white precipitate; and *lead acetate*, a white precipitate much less soluble in water than the chloride. *Palladium nitrate* produces in solutions of bromides not containing chlorine, a black precipitate of bromide. *Palladium chloride* produces no precipitate; neither does the nitrate, if soluble chlorides are present.

Bromides unite with each other in the same manner as chlorides; also with oxides, sulphides, and ammonia.

Iodides.—These compounds are obtained by processes similar to those which yield the chlorides and bromides. Many metals unite directly with iodine. Potassium and sodium iodides exist in sea-water and in many salt-springs; silver iodide occurs as a natural mineral.

Metallic iodides are analogous to the bromides and chlorides in composition and properties. But few of them are decomposed by heat alone; the oxides of gold, silver, platinum, and palladium, however, give up their iodine when heated.

Most metallic iodides are perfectly soluble in water; but lead iodide is very slightly soluble, and the iodides of mercury and silver are quite insoluble.

Solutions of iodides evaporated out of contact of air, generally leave anhydrous metallic iodides, which partly separate in the crystalline form before the water is wholly driven off. The iodides of the earth-metals, however, are resolved, on evaporation, into the earthy oxides and hydriodic acid which escapes. A very small quantity of *chlorine* colors the solution yellow or brown, by partial decomposition; and a somewhat larger quantity takes up the whole of the metal, forming a chloride, and separates the iodine, which then gives a blue color with starch; a still larger quantity of chlorine gives the liquid a paler color, and converts the separated iodine into trichloride of iodine, which does not give a blue color with starch, and frequently enters into combination with the metallic chloride produced. Strong *sulphuric acid* and somewhat concentrated *nitric acid* color the solution yellow or brown; and if the quantity of the iodide is large, and the solution much concentrated or heated, they liberate iodine, which partly escapes in violet vapor. *Starch* mixed with the solution, even if it be very dilute, is turned blue—permanently when the decomposition is effected by sulphuric acid; for a time only when it is effected by nitric acid, especially if that acid be added in large quantity.

The aqueous solution of an iodide gives a brown precipitate with salts of *bismuth*; orange-yellow with *lead* salts; dirty-white with *cuprous* salts, and also with *cupric* salts, especially on the addition of sulphurous acid; greenish-yellow with *mercurous* salts; scarlet with *mercuric* salts; yellowish-white with *silver* salts; lemon-yellow with *gold* salts; brown with *platinic* salts—first, however, turning the liquid dark-brown-red; and black with salts of *palladium*, even when extremely dilute. All these precipitates consist of metallic iodides, many of them soluble in excess of the soluble iodide: the silver precipitate is insoluble in nitric acid, and very little soluble in ammonia.

Metallic iodides unite with one another, forming double iodides, analogous to the double chlorides; they also absorb ammonia gas in definite proportions. Some of them, as those of antimony and tellurium, unite with the oxides of the corresponding metals, forming oxyiodides.

Fluorides.—These compounds are formed—1. By heating hydrofluoric acid with certain metals. 2. By the action of that acid on metallic oxides. 3. By heating electro-negative metals—antimony, for example—with fluoride of lead or fluoride of mercury. 4. Volatile metallic fluorides

may be prepared by heating fluor-spar with sulphuric acid, and the oxide of the metal.

Fluorides have no metallic lustre; most of them are easily fusible, and for the most part resemble the chlorides. They are not decomposed by ignition, either alone or when mixed with charcoal. When ignited in contact with the air, in a flame which contains aqueous vapor, many of them are converted into oxides, while the fluorine is given off as hydrofluoric acid. All fluorides are decomposed by *chlorine*, and converted into chlorides. They are not decomposed by *phosphoric oxide*, unless silica is present. They are decomposed at a gentle heat by strong sulphuric acid, with formation of a metallic sulphate and evolution of hydrofluoric acid.

The fluorides of tin and silver are easily soluble in water; those of potassium, sodium, and iron are sparingly soluble; those of strontium and cadmium very slightly soluble, and the rest insoluble. The solutions of ammonium, potassium, and sodium fluoride have an alkaline reaction. The aqueous solutions of fluorides corrode glass vessels in which they are kept or evaporated. They form, with soluble *calcium-salts*, a precipitate of calcium fluoride, in the form of a transparent jelly, which is scarcely visible, because its refractive power is nearly the same as that of the liquid; the addition of ammonia makes it plainer. This precipitate, if it does not contain silica, dissolves with difficulty in hydrochloric or nitric acid, and is re-precipitated by ammonia. The aqueous fluorides give a pulverulent precipitate with lead acetate.

The fluorides of antimony, arsenic, chromium, mercury, niobium, osmium, tantalum, tin, titanium, tungsten, and zinc are volatile without decomposition.

Fluorine has a great tendency to form double salts, consisting of a fluoride of a basic or positive metal united with the fluoride of hydrogen, boron, silicon, tin, titanium, zirconium, etc., *e. g.*—

| | | |
|---------------------------|-------|---|
| Potassium hydrofluoride | . . . | $\text{KHF}_2 = \text{KF.HF}$ |
| Potassium borofluoride | . . . | $\text{KBF}_4 = \text{KF.BF}_3$ |
| Potassium silicofluoride | . . . | $\text{K}_2\text{SiF}_6 = 2\text{KF.SiF}_5$ |
| Potassium titanofluoride | . . . | $\text{K}_2\text{TiF}_6 = 2\text{KF.TiF}_5$ |
| Potassium stannofluoride | . . . | $\text{K}_2\text{SnF}_6 = 2\text{KF.SnF}_5$ |
| Potassium zirconofluoride | . . . | $\text{K}_2\text{ZrF}_6 = 2\text{KF.ZrF}_5$ |

The four classes of compounds just described, the chlorides, bromides, iodides, and fluorides, form a group often designated as haloid compounds or haloid* salts, from their analogy to sodium chloride or sea salt, which may be regarded as a type of them all. The elements, chlorine, bromine, iodine, and fluorine, are called halogens.

Cyanides.—Closely related to these haloid compounds are the cyanides, formed by the union of metals with the group CN, cyanogen, which is a monatomic radicle derived from the saturated molecule, $\text{C} \equiv \text{N}-\text{H}$ (hydrocyanic acid), by abstraction of H; in short, the cyanides may be regarded as chlorides having the element Cl replaced by the compound radicle CN (p. 175).

Some metals—potassium among the number—are converted into cyanides by heating them in cyanogen gas or vapor of hydrocyanic acid. The cyanides of the alkali-metals are also formed (together with cyanates) by passing cyanogen gas over the heated hydroxides or carbonates of the same metals; potassium cyanide also, by passing nitrogen gas over a mixture of charcoal and hydroxide or carbonate of potassium at a bright red

* From ἅλα, the sea.

Heat. Cyanides are formed abundantly when nitrogenous organic compounds are heated with fixed alkalis. Other modes of formation will be mentioned hereafter.

The cyanides of the alkali-metals, and of barium, strontium, calcium, magnesium, and mercury, are soluble in water, and may be produced by heating the corresponding oxides or hydroxides with hydrocyanic acid. Nearly all other metallic cyanides are insoluble, and are obtained by precipitation from the soluble cyanides.

The cyanides of the alkali-metals sustain a red heat without decomposition, provided air and moisture be excluded. The cyanides of many of the heavy metals, as lead, iron, cobalt, nickel, and copper, under these circumstances, give off all their nitrogen as gas, and leave a metallic carbonate; mercuric cyanide is resolved into mercury and cyanogen gas; silver cyanide gives off half its cyanogen as gas. Most cyanides, when heated with dilute acids, give off their cyanogen as hydrocyanic acid.

Cyanides have a strong tendency to unite with one another, forming double cyanides. The most important of these are the double cyanides of iron and potassium, namely, *potassio-ferrous cyanide*, $\text{Fe}''\text{K}_4(\text{CN})_6$, commonly called yellow prussiate of potash; and *potassio-ferric cyanide*, $\text{Fe}'''\text{K}_4(\text{CN})_6$, commonly called red prussiate of potash. Both these are splendidly crystalline salts, which dissolve easily in water, and form highly characteristic precipitates with many metallic salts. These salts, with the other cyanides, will be more fully described under "Organic Chemistry;" but they are mentioned here, on account of their frequent use in the qualitative analysis of metallic solutions.

Oxides.—All metals combine with oxygen, and most of them in regular proportions. In almost all cases oxides are formed corresponding in composition with the chlorides, one atom of oxygen taking the place of two atoms of chlorine. Many metals also form oxides to which no chlorine analogues are known; thus lead, which forms only one chloride, PbCl_2 , forms, in addition to the monoxide, PbO , a dioxide, PbO_2 , besides oxides of intermediate composition; osmium also, the highest chloride of which is OsCl_6 , forms, in addition to the dioxide, a trioxide and a tetroxide. This arises from the fact that any number of atoms of oxygen or other dyad element may enter into a compound without disturbing the balance of equivalency (p. 237).

Just as chlorides are derived by substitution from hydrochloric acid, HCl (p. 277), so likewise may oxides be derived from one or more molecules of water, H_2O ; but as the molecule of water contains two hydrogen-atoms, the replacement of the hydrogen may, as already explained (p. 237), be either total or partial, the product in the first case being an anhydrous metallic oxide, and in the second a hydrated oxide or hydroxide, in which the oxygen is associated both with hydrogen and with metal; in this manner the following hydroxides and anhydrous oxides may be constituted:—

| Type. | Hydroxides. | Oxides. |
|-----------------------------------|--|--|
| H_2O | KHO | K_2O
Ba''O |
| H_4O_2 | $\text{Ba}'''\text{H}_2\text{O}_2$
$\text{Bi}'''\text{HO}_2$ | $\text{Sn}^{\text{iv}}\text{O}_2$ |
| H_6O_3 | $\text{As}^{\text{v}}\text{HO}_3$
$\text{Sn}^{\text{iv}}\text{H}_2\text{O}_3$ | $\text{Sb}^{\text{v}}\text{O}_3$
$\text{W}^{\text{vi}}\text{O}_3$ |
| H_8O_4 | $\text{Zr}^{\text{iv}}\text{H}_4\text{O}_4$ | |
| H_{10}O_5 | | $\text{Sb}^{\text{v}}\text{O}_5$ |

It may be observed that the hydroxides of artiad metals contain the elements of a molecule of the corresponding anhydrous oxide, and of one or more molecules of water, and may therefore also be regarded as hydrates: thus—

| | |
|---------------------------------------|------------------------------|
| Barium hydroxide or hydrate . . . | $Ba''H_2O_2 = Ba''(O.H_2O)$ |
| Stannic " " . . . | $Sn''H_2O_3 = Sn''O_2.H_2O$ |
| Zirconium " " . . . | $Zr''H_4O_4 = Zr''O_2.2H_2O$ |

But the hydroxide of a perissad metal contains in its molecule only half the number of atoms required to make up a molecule of oxide together with a molecule of water; thus—

| | |
|-------------------------------|--|
| Potassium hydroxide | $KHO = \frac{1}{2}(K_2O.H_2O)$ |
| Bismuth hydroxide | $Bi'''HO_2 = \frac{1}{2}(Bi'''O_3.H_2O)$ |
| Arsenic hydroxide | $As'HO_3 = \frac{1}{2}(As'_2O_3.H_2O)$ |

These perissad hydroxides cannot, therefore, be correctly regarded as hydrates, that is, as compounds of anhydrous oxide and water.

Many metallic oxides occur as natural minerals, and some, especially those of iron, tin, and copper, in large quantities, forming ores from which the metals are extracted.

All metals, except gold, platinum, iridium, rhodium, and ruthenium, are capable of uniting directly with oxygen. Some, as potassium, sodium, and barium, oxidize rapidly on exposure to the air at ordinary temperatures, and decompose water with energy. Most metals, however, when in the massive state, remain perfectly bright and unacted on in dry air or oxygen gas, but oxidize slowly when moisture is present; such is the case with iron, zinc, and lead. Some of the ordinarily permanent metals, when in a very finely divided state, as lead when obtained by ignition of its tartrate, and iron reduced from its oxide by ignition in hydrogen gas, take fire and oxidize spontaneously as soon as they come in contact with the air. Lead, iron, copper, and the volatile metals, arsenic, antimony, zinc, cadmium, and mercury, are converted into oxides when heated in air or oxygen. Many metals, especially at a red heat, are readily oxidized by water or steam. A very general method of preparing metallic oxides is to subject the corresponding hydroxides, carbonates, nitrates, sulphates, or any oxygen-salts containing volatile acids, to the action of heat.

Oxides are for the most part opaque earthy bodies, destitute of metallic lustre. The majority of them are fusible; those of lead and bismuth at a low red heat; those of copper and iron at a white heat; those of barium and aluminium before the oxy-hydrogen blow-pipe; while calcium oxide or lime does not fuse at any temperature to which it has yet been subjected. Oxides are, for the most part, much less fusible than the uncombined metals. Osmium tetroxide, and the trioxides of arsenic and antimony, are readily volatile.

A greater or lesser degree of heat effects the decomposition of many metallic oxides. Those of gold, platinum, silver, and mercury are reduced to the metallic or reguline state by an incipient red heat. At a somewhat higher temperature, the higher oxides of barium, cobalt, nickel, and lead are reduced to the state of monoxides; while the trimetallic tetroxides of manganese and iron, Mn_2O_4 and Fe_3O_4 , are produced by exposing manganese dioxide, MnO_2 , and iron sesquioxide, Fe_2O_3 , respectively to a still stronger heat. By gentle ignition, arsenic pentoxide is reduced to the state of trioxide, and chromium trioxide to sesquioxide.

The superior oxides of the metals are easily reduced to a lower state of oxidation by treatment with a current of *hydrogen gas* at a more or less elevated temperature. At a higher degree of heat, hydrogen gas will transform to the reguline state all metallic oxides except the sesquioxides of

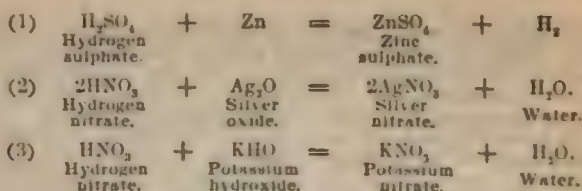
aluminium and chromium, and the monoxides of manganese, magnesium, barium, strontium, calcium, lithium, sodium, and potassium. The temperature necessary to enable hydrogen to effect the decomposition of some of these is comparatively low. Thus metallic iron may be reduced from its oxides by hydrogen gas at a heat considerably below redness. Carbon, at red or white heat, is a still more powerful deoxidizing agent than hydrogen, and seems to be capable of completely reducing all metallic oxides whatsoever. The oxidizable metals in general act as reducing agents.

Chlorine decomposes all metallic oxides, except those of the earth-metals, converting them into chlorides, and expelling the oxygen. With silver and this reaction takes place at ordinary temperatures; with the alkalis and the alkaline earths, at a full red heat. Sulphur, at high temperatures, decomposes most metallic oxides; with many oxides—those of silver, mercury, lead, and copper, for instance—metallic sulphides and sulphur fumes are produced; with the highly basulous oxides, the products are metallic sulphate and sulphide. There are some oxides upon which sulphur exerts no action. Of these the principal are magnesia, alumina, chromia, stannic, and titanio oxides. By boiling sulphur with soluble hydroxides, mixtures of polysulphide and thiosulphate are produced. With the exception of magnesia, alumina, and chromic oxide, most metallic oxides can absorb sulphuretted hydrogen, to form metallic sulphide or hydrosulphide and water.

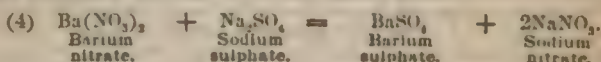
Oxygen-salts or Oxy-salts.—It has been already explained in the chapter on Oxygen (p. 125) that oxides may be divided into three classes, *acid*, *neutral*, and *basic*; the first and third being capable of uniting with one another in definite proportions, and forming compounds called salts. The most characteristic of the acid oxides are those of certain metalloids, as nitrogen, sulphur, and phosphorus, which unite readily with water or the elements of water, forming compounds called oxygen-acids, distinguished by sour taste, solubility in water, and the power of coloring certain vegetable blue colors. The most characteristic of the basic oxides, on the other hand, are those of the alkali-metals and alkaline earth-metals (p. 273), which likewise dissolve in water, but form alkaline solutions, possessing in an eminent degree the power of neutralizing acids and forming salts with them. The same power is exhibited more or less by the monoxides of most other metals, as zinc, iron, copper, manganese, etc., and by the sesquioxides of aluminium, iron, chromium, and others. The higher oxides of several of these metals—the trioxides of chromium, for example—exhibit acid characters, being capable of forming salts with the more basic oxides; and some metals, as arsenic, antimony, selenium, and tantalum, form only acid oxides.

In some cases salts are formed by the direct combination of an acid and a basic oxide. Thus, when vapor of sulphuric oxide, SO_3 , is passed over red hot barium oxide, BaO , the two combine together, and form barium sulphate, $\text{BaO} \cdot \text{SO}_3$, or BaSO_4 . Silicic oxide, SiO_2 , phosphoric oxide, P_2O_5 , boracic oxide, B_2O_3 , and other acid oxides capable of withstanding a high temperature without decomposing or volatilizing, likewise unite with basic oxides when heated with them, and form salts.

But in the majority of cases metallic salts are formed by substitution, or interchange of metal for hydrogen, or of one metal for another. It is clear, indeed, that any metallic salt (zinc sulphate, $\text{ZnO} \cdot \text{SO}_3$, for example) may be derived from the corresponding acid or hydrogen salt ($\text{H}_2\text{O} \cdot \text{SO}_3$) by substitution of a metal for an equivalent quantity of hydrogen. Accordingly, metallic salts are frequently produced by the action of an acid on a metal or a metallic oxide or hydroxide, thus—

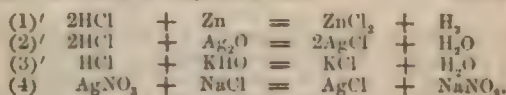


In the instances represented by these equations, the metallic salts formed are soluble in water. Insoluble salts are frequently prepared by interchange of the metals between two soluble salts; thus—



In this case the barium sulphate, being insoluble, is precipitated, while the sodium nitrate remains in solution.

In all these reactions, hydrochloric acid or a metallic chloride might be substituted for the oxygen-acid or oxygen-salt, without the slightest alteration in the mode of action, the product formed in each case being a chloride instead of a nitrate or sulphate; thus—



From all these considerations it appears that oxygen-salts may be regarded, either as compounds of acid oxides with basic oxides, or as analogous in composition to chlorides,—that is to say, as compounds of a metal with a radicle or group of elements, such as NO_3 (*nitric*) in the nitrates, SO_4 (*sulphic*), in the sulphates, discharging functions similar to those of chlorine, and capable, like that element, of passing unchanged from one compound to another.

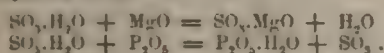
For many years, indeed, it was a subject of discussion among chemists, whether the former or the latter of these views should be regarded as representing the *actual* constitution of oxygen-salts. Berzelius divided salts into two classes: 1. Haloid salts, comprising, as already mentioned, the chlorides, bromides, iodides, and fluorides, which are compounds of a metal with a monad metallic element. 2. Amphid salts, consisting of an acid or electro-negative oxide, sulphide, selenide, or telluride, with a basic or electro-positive compound of the same kind; such as potassium arsenate, $3\text{K}_2\text{O}.\text{As}_2\text{O}_5$; potassium sulpharsenate, $3\text{K}_2\text{S}.\text{As}_2\text{S}_5$; potassium seleniophosphate, $2\text{K}_2\text{Se}.\text{P}_2\text{Se}_5$, etc.

Davy, on the other hand, observing the close analogy between the reactions of chlorides, on the one hand, and of oxygen salts, such as sulphates, nitrates, etc., on the other, suggested that the latter might be regarded, like the former, as compounds of metals with acid electro-negative radicles, the only difference being, that in the former the acid radicle is an elementary body, Cl, Br, etc., whereas in the latter it is a compound, as SO_4 , NO_3 , PO_4 , etc. This was called the *binary theory of salts*; it was supported by many ingenious arguments by its proposer and several contemporary chemists; in later years also by Liebig, and by Daniell and Miller, who observed that the mode of decomposition of salts by the electric current is more easily represented by this theory than by the older one (p. 260).

At the present day, the relative merits of these two theories are not regarded as a point of very great importance. Chemists, in fact, no longer attempt to construct formulæ which shall represent the actual arrangement of atoms in a compound, the formulæ now in use being rather intended to exhibit, first, the balance or neutralization of the units of equivalency or atomicity of the several elements contained in a compound (p. 253); and, secondly, the manner in which any compound or group of atoms splits up into subordinate groups under the influence of different reagents. According to the latter view, a compound containing three or more elementary atoms may be represented by different formulæ corresponding with the several ways in which it decomposes. Thus hydrogen sulphate or sulphuric acid, H_2SO_4 , may be represented by either of the following formulæ:—

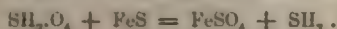
1. H_2SO_4 , which represents the separation of hydrogen and formation of a metallic sulphate, by the action of zinc, etc.; this is the formula corresponding with the binary theory of salts.

2. $\text{SO}_2\text{H}_2\text{O}$. This formula represents the formation of the acid by direct hydration of sulphuric oxide; the separation of water and formation of a metallic sulphate by the action of magnesia and other anhydrous oxides; and the separation of sulphuric oxide and formation of phosphoric acid by the action of phosphoric oxide:—



3. $\text{SO}_2\text{O}_2\text{H}_2$, or $\text{SO}_2(\text{OH})_2$. This formula represents such reactions as the elimination of hydrogen dioxide by the action of barium dioxide, BaO_2 .

4. SH_2O_4 . This formula represents the formation of sulphuric acid by direct oxidation of hydrogen sulphide, SH_2 , and the elimination of the latter by the action of ferrous sulphide:—

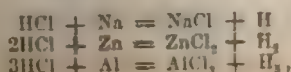


Formulæ of the third of these types, like $\text{SO}_2(\text{OH})_2$, which represent oxygen-acids as compounds of hydroxyl with certain acid radicles, as SO_2'' (sulphuryl), CO'' (carbonyl), PO''' (phosphoryl), etc., correspond with a great variety of reactions, and are of very frequent use. They exhibit in particular the relation of the oxygen-acids (hydroxylates) to the corresponding chlorides, e.g.:—

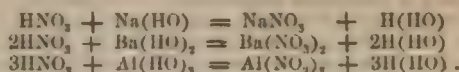


Basicity of Acids.—*Normal, Acid and Double Salts.*—Acids are monobasic, bibasic, tribasic, etc., according as they contain one or more atoms of hydrogen replaceable by metals; thus nitric acid, HNO_3 , and hydrochloric acid, HCl , are monobasic; sulphuric acid, H_2SO_4 , is bibasic; phosphoric acid, H_3PO_4 , is tribasic.

Monobasic acids form but one class of salts by substitution, the metal taking the place of the hydrogen in one, two, or three molecules of the acid, according to its equivalent value or atomicity; thus the action of hydrochloric acid on sodium, zinc, and aluminium is represented by the equations:—



and that of nitric acid on the hydroxides of the same metals by the equations :—



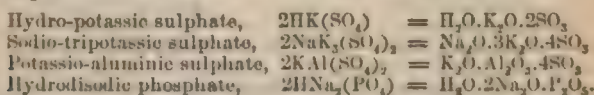
Bibasic acids, on the other hand, form two classes of salts, viz., *primary* or *acid salts*, in which half the hydrogen is replaced by a metal; and *secondary salts*, in which the whole of the hydrogen is thus replaced, the salt being called *normal* or *neutral*, if it contains one metal, and *double* if it contains two metals; thus :—

| | |
|--|--|
| From H_2SO_4 is derived KHSO_4 | { hydro-potassic sulphate, primary, or |
| “ “ “ K_2SO_4 | { acid potassium sulphate, |
| “ “ “ BaSO_4 | { bipotassic sulphate, secondary, or |
| “ “ “ $\text{NaK}(\text{SO}_4)_2$ | { normal sulphate, |
| “ $2\text{H}_2\text{SO}_4$ “ $\text{NaK}_2(\text{SO}_4)_2$ | barium sulphate, |
| “ “ “ $\text{KAl}(\text{SO}_4)_2$ | sodio-tripotassic sulphate, |
| “ $3\text{H}_2\text{SO}_4$ “ $\text{Al}_2(\text{SO}_4)_3$ | potassio-aluminic sulphate, |
| | normal aluminium sulphate. |

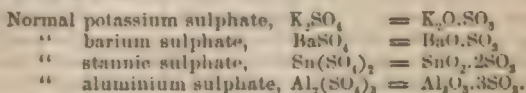
Tribasic acids in like manner form two classes of acid salts, *primary* or *secondary*, according as one-third or two-thirds of the hydrogen is replaced by a metal; also *tertiary salts*, including *normal* and *double* or *triple salts*, in which the hydrogen is wholly replaced by one or more metals; in quadribasic acids the variety is of course still greater.

The use of the terminations *ous* and *ic*, as applied to salts, has already been explained. We have only further to observe in this place that when a metal forms but one class of salts, it is for the most part better to designate those salts by the name of the metal itself than by an adjective ending in *ic*; thus *potassium nitrate*, and *lead sulphate*, are mostly to be preferred to *potassic nitrate* and *plumbic sulphate*. But in naming double salts, and in many cases where a numeral prefix is required, the names ending in *ic* are more euphonious; thus *tripotassic phosphate* sounds better than *trilead phosphate*, and *hydrodisodic phosphate* is certainly better than *hydrogen and disodium phosphate*; but there is no occasion for a rigid adherence to either system.

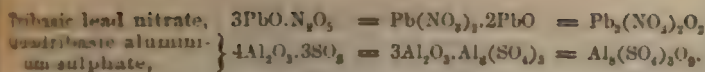
All oxygen-salts may also be represented as compounds of an acid oxide with one or more molecules of the same or different basic oxides, including water, *e. g.* :



When a normal oxygen-salt is thus formulated, it is easy to see that the number of molecules of acid oxide contained in its molecule is equal to the number of oxygen-atoms in the base; thus :



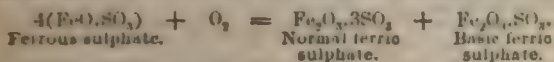
When the proportion of acid oxide is less than this, the salt is called *basic*; such salts may be regarded as compounds of a normal salt with one or more molecules of basic oxide, or as derived from normal salts by *substitution of oxygen* for an equivalent quantity of the acid radicle; thus :



The last mode of formulation exhibits the analogy of these basic oxides to the oxychlorides, oxyiodides, etc.; thus the basic lead nitrate, $\text{Pb}(\text{NO}_3)_2\text{O}_2$, just mentioned, is analogous to the oxychloride of that metal, $\text{Pb}_2\text{Cl}_2\text{O}_2$, which occurs native as mendipite.

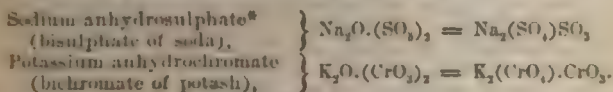
The terms basic and acid are sometimes applied to salts with reference to their action on vegetable colors. The normal salts formed by the union of the stronger acids with the alkalis and alkaline earths, such as potassium sulphate, K_2SO_4 , barium nitrate, $\text{Ba}(\text{NO}_3)_2$, etc., are perfectly neutral to vegetable colors, but most other normal salts exhibit either an acid or an alkaline reaction; thus ferrous sulphate, cupric sulphate, silver nitrate, and many others, redden litmus, while the normal carbonates and phosphates of the alkali-metals exhibit a decided alkaline reaction. It is clear, then, that the action of a salt on vegetable colors bears no definite relation to its composition: hence the term *normal*, as applied to salts in which the basic hydrogen of the acid is wholly replaced, is preferable to *neutral*, and the terms *basic* and *acid*, as applied to salts, are best used in the manner above explained with reference to their composition.

When a normal salt containing a monoxide passes by oxidation to a salt containing a sesquioxide, dioxide, or trioxide, the quantity of acid present is no longer sufficient to saturate the base. Thus, when a solution of ferrous sulphate, FeSO_4 , or $\text{FeO} \cdot \text{SO}_3$ (common green vitriol), is exposed to the air it absorbs oxygen, and an insoluble ferric salt is produced containing an excess of base, while normal ferric sulphate remains in solution:



These basic salts are very often insoluble in water.

Salts containing a proportion of acid oxide larger than is sufficient to form a neutral compound are called anhydro-salts (sometimes, though improperly, acid salts); they may evidently be regarded as compounds of a normal salt with excess of acid oxide; e. g.:



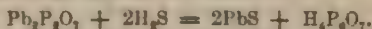
The following is a list of the most important inorganic acids arranged according to their basicity:—

Monobasic Acids.

| | | | |
|---------------------------|------------------------------------|------------------------|-----------------|
| Hydrochloric | HCl | Boric | HBO_3 |
| Hydrobromic | HBr | Antimonic | HSbO_3 |
| Hydroiodic | HI | Hypochlorous | HClO |
| Hydrofluoric | HF | Chlorous | HClO_2 |
| Nitrous | HNO_2 | Chloric | HClO_3 |
| Nitric | HNO_3 | Perehloric | HClO_4 |
| Hyposulphurous | $\text{H}_2\text{SiH}_2\text{O}_2$ | Bromic | HBrO_3 |
| Hypophosphorous | $\text{H}(\text{PH}_2\text{O}_2)$ | Iodic | HIO_3 |
| Metaphosphoric | HPO_3 | Periodic | HIO_4 |

* The so-called "anhydrosulphates" are now regarded as salts of a distinct acid, pyrosulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$ (p. 197).

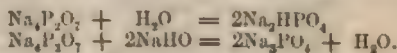
and lead pyrophosphate decomposed by hydrogen sulphide yields hydrogen pyrophosphate or pyrophosphoric acid :—



Pyrophosphoric acid is distinguished from metaphosphoric acid by not coagulating albumin and not precipitating neutral solutions of barium or silver salts, and from orthophosphoric acid by producing a white, instead of a yellow, precipitate with silver nitrate.

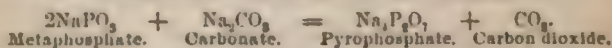
Pyrophosphates are easily converted into metaphosphates and orthophosphates, and *vice versa*, by addition or abstraction of water or a metallic base.

a. The production of a pyrophosphate from an orthophosphate by loss of water has been already mentioned.—*β*. Conversely, when a pyrophosphate is heated with water or a base, it becomes an orthophosphate, *e. g.* :—



In like manner, orthophosphoric acid heated to 215° is almost entirely converted into pyrophosphoric acid : $2\text{H}_3\text{PO}_4 - \text{H}_2\text{O} = \text{H}_4\text{P}_2\text{O}_7$; and conversely, when pyrophosphoric acid is boiled with water, it is transformed into orthophosphoric acid.

γ. Pyrophosphoric acid heated to dull redness is converted into metaphosphoric acid : $\text{H}_4\text{P}_2\text{O}_7 - \text{H}_2\text{O} = 2\text{HPO}_3$. The converse reaction is not easily effected, inasmuch as metaphosphoric acid by absorbing water generally passes directly to the state of orthophosphoric acid. Peligot, however, observed the formation of pyrophosphoric from metaphosphoric acid by very slow absorption of water.—*δ*. When a metallic metaphosphate is treated with a proper proportion of a hydroxide, oxide, or carbonate, it is converted into a pyrophosphate; thus :—



Fleitmann and Henneberg, by fusing together a molecule of sodium pyrophosphate, $\text{Na}_2\text{PO}_4.\text{NaPO}_3$, with two molecules of metaphosphate, NaPO_3 , obtained a salt having the composition, $\text{Na}_2\text{PO}_4.3\text{NaPO}_3 = \text{Na}_8\text{P}_4\text{O}_{12}$, which is soluble without decomposition in a small quantity of hot water, and crystallizes from its solution by evaporation over oil of vitriol. An excess of hot water decomposes it, but its cold aqueous solution is moderately permanent. Insoluble phosphates of similar composition may be obtained from the sodium-salt by double decomposition. Fleitmann and Henneberg obtained another crystallizable but very insoluble salt, having the composition, $\text{Na}_2\text{PO}_4.9\text{NaPO}_3 = \text{Na}_{12}\text{P}_{10}\text{O}_{31}$, by fusing together one molecule of sodium pyrophosphate with eight molecules of the metaphosphate; and insoluble phosphates of similar constitution were obtained from it by double decomposition.

The comparative composition of these different phosphates is best shown by representing them as compounds of phosphoric oxide with metallic oxide, and assigning to them all the quantity of base contained in the most complex member of the series; thus—

| | |
|---|--|
| Orthophosphate | $6\text{Na}_2\text{O}.2\text{P}_2\text{O}_5 = 4\text{Na}_4\text{PO}_4$ |
| Pyrophosphate | $6\text{Na}_2\text{O}.3\text{P}_2\text{O}_5 = 3\text{Na}_6\text{P}_3\text{O}_7$ |
| Fleitmann and Henneberg's phosphate (a) | $6\text{Na}_2\text{O}.4\text{P}_2\text{O}_5 = 2\text{Na}_8\text{P}_4\text{O}_{12}$ |
| " " " (b) | $6\text{Na}_2\text{O}.5\text{P}_2\text{O}_5 = \text{Na}_{10}\text{P}_5\text{O}_{15}$ |
| Metaphosphate | $6\text{Na}_2\text{O}.6\text{P}_2\text{O}_5 = 12\text{NaPO}_3$ |

Metallio Sulphides.—These compounds correspond, for the most part, in composition with the oxides: thus, there are two sulphides of arsenic, As_2S_3 and As_2S_5 , corresponding with the oxides, As_2O_3 and As_2O_5 ; also, two sulphides of mercury, Hg_2S and HgS , analogous to the oxides, Hg_2O and HgO . Occasionally, however, we meet with oxides to which there are no corresponding sulphides (manganese dioxide, for example), and more frequently sulphides to which there are no corresponding oxides, the most remarkable of which are, perhaps, the alkaline polysulphides. Potassium, for example, forms the series of sulphides, K_2S , K_2S_2 , K_2S_3 , K_2S_4 , and K_2S_5 , the third and fifth of which have no analogues in the oxygen series.

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Many metallic sulphides occur as natural minerals, especially the sulphides of lead, copper, and mercury, which afford valuable ores for the extraction of the metals, and iron bisulphide or iron pyrites, FeS_2 , which is largely used as a source of sulphur, and for the preparation of ferrous sulphates.

Sulphides are formed artificially by heating metals with sulphur; by the action of metals on gaseous hydrogen sulphide; by the reduction of sulphates with hydrogen or charcoal; by heating metallic oxides in contact with gaseous hydrogen sulphide or vapor of carbon bisulphide; and by precipitation of metallic solutions with hydrogen sulphide or a sulphide of alkali-metal. Some metals, as copper, lead, silver, bismuth, mercury, and cadmium, are precipitated from their acid solutions by hydrogen sulphide, passed into them as gas, or added in aqueous solution, the sulphides of these metals being insoluble in dilute acids; others, as iron, cobalt, nickel, manganese, zinc, and uranium, form sulphides which are soluble in acids, and these are precipitated by hydrogen sulphide only from alkaline solutions, or by ammonium or potassium sulphide from neutral solutions. Many of these sulphides exhibit characteristic colors, which serve as indications of the presence of the respective metals in solution (p. 200).

Metallic sulphides are also formed by the reduction of sulphates with organic substances; many native sulphides have doubtless been formed in this way.

The physical characters of some metallic sulphides closely resemble those of the metals in certain particulars, such as the peculiar opacity, lustre, and density, especially when they are in a crystalline condition. They are generally crystallizable, brittle, and of a gray, pale yellow, or dark brown color. The sulphides of the alkali-metals are soluble in water; most of the others are insoluble. They are more frequently fusible than the corresponding oxides, and some are volatilizable, as mercury sulphide and arsenic sulphide.

Many sulphides, when heated out of contact with atmospheric air, do not undergo any decomposition; this is the case chiefly with those containing the smallest proportions of sulphur, such as the monosulphides of iron and zinc. Sulphides containing larger proportions of sulphur are partially decomposed by heat, losing part of their sulphur, and being converted into lower sulphides; as in the case of iron bisulphide. The sulphides of gold and platinum are completely reduced by heat.

By the simultaneous action of heat and of substances capable of combining with sulphur, some sulphides may be decomposed. Thus, for

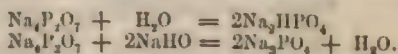
and lead pyrophosphate decomposed by hydrogen sulphide yields hydrogen pyrophosphate or pyrophosphoric acid :—



Pyrophosphoric acid is distinguished from metaphosphoric acid by not coagulating albumin and not precipitating neutral solutions of barium or silver salts, and from orthophosphoric acid by producing a white, instead of a yellow, precipitate with silver nitrate.

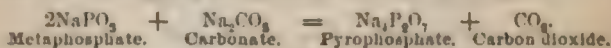
Pyrophosphates are easily converted into metaphosphates and orthophosphates, and *vice versa*, by addition or abstraction of water or a metallic base.

a. The production of a pyrophosphate from an orthophosphate by loss of water has been already mentioned.—*b*. Conversely, when a pyrophosphate is heated with water or a base, it becomes an orthophosphate, *c. g.* :—



In like manner, orthophosphoric acid heated to 215° is almost entirely converted into pyrophosphoric acid : $2\text{H}_3\text{PO}_4 - \text{H}_2\text{O} = \text{H}_4\text{P}_2\text{O}_7$; and conversely, when pyrophosphoric acid is boiled with water, it is transformed into orthophosphoric acid.

g. Pyrophosphoric acid heated to dull redness is converted into metaphosphoric acid : $\text{H}_4\text{P}_2\text{O}_7 - \text{H}_2\text{O} = 2\text{HPO}_3$. The converse reaction is not easily effected, inasmuch as metaphosphoric acid by absorbing water generally passes directly to the state of orthophosphoric acid. Peligot, however, observed the formation of pyrophosphoric from metaphosphoric acid by very slow absorption of water.—*h*. When a metallic metaphosphate is treated with a proper proportion of a hydroxide, oxide, or carbonate, it is converted into a pyrophosphate; thus :—



Fleitmann and Henneberg, by fusing together a molecule of sodium pyrophosphate, $\text{Na}_2\text{PO}_4.\text{NaPO}_3$, with two molecules of metaphosphate, NaPO_3 , obtained a salt having the composition, $\text{Na}_2\text{PO}_4.3\text{NaPO}_3 = \text{Na}_8\text{P}_5\text{O}_{13}$, which is soluble without decomposition in a small quantity of hot water, and crystallizes from its solution by evaporation over oil of vitriol. An excess of hot water decomposes it, but its cold aqueous solution is moderately permanent. Insoluble phosphates of similar composition may be obtained from the sodium-salt by double decomposition. Fleitmann and Henneberg obtained another crystallizable but very insoluble salt, having the composition, $\text{Na}_2\text{PO}_4.9\text{NaPO}_3 = \text{Na}_{12}\text{P}_{10}\text{O}_{31}$, by fusing together one molecule of sodium pyrophosphate with eight molecules of the metaphosphate; and insoluble phosphates of similar constitution were obtained from it by double decomposition.

The comparative composition of these different phosphates is best shown by representing them as compounds of phosphoric oxide with metallic oxide, and assigning to them all the quantity of base contained in the most complex member of the series; thus—

| | |
|--|---|
| Orthophosphate | $6\text{Na}_2\text{O}.2\text{P}_2\text{O}_5 = 4\text{Na}_3\text{PO}_4$ |
| Pyrophosphate | $6\text{Na}_2\text{O}.3\text{P}_2\text{O}_5 = 3\text{Na}_4\text{P}_2\text{O}_7$ |
| Fleitmann and Henneberg's phosphate (<i>a</i>) | $6\text{Na}_2\text{O}.4\text{P}_2\text{O}_5 = 2\text{Na}_8\text{P}_5\text{O}_{13}$ |
| " " " " (<i>b</i>) | $6\text{Na}_2\text{O}.5\text{P}_2\text{O}_5 = \text{Na}_{12}\text{P}_{10}\text{O}_{31}$ |
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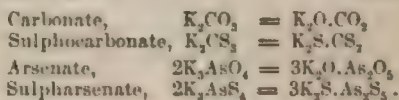
instance, silver, copper, bismuth, tin, and antimony sulphides are reduced by hydrogen; copper, lead, mercury, and antimony sulphides are reduced by heating with iron.

Sulphides which are not reduced by heat alone are always decomposed when heated in contact with oxygen or atmospheric air. Those of the alkali-metals and earth-metals are converted into sulphates by this means. Zinc, iron, manganese, copper, lead, and bismuth sulphides are converted into oxides, and sulphurous oxide is produced: but when the temperature is not above dull redness, some sulphate is formed by direct oxidation. Mercury and silver sulphides are completely reduced to the metallic state. Some native sulphides gradually undergo alteration by mere exposure to the air: but it is then generally limited to the production of sulphates, unless the oxidation takes place so rapidly that the heat generated is sufficient to decompose the sulphate first produced. In the production of some metals for use in the arts, the separation of sulphur from the native minerals is effected chiefly by means of this action in the operation of roasting.

Metallic sulphides are decomposed in like manner when heated with metallic oxides in suitable proportions, yielding sulphurous oxide and the metal of both the sulphide and oxide. Lead is reduced from the native sulphide in this manner.

Many metallic sulphides are decomposed by acids in presence of water, sulphuretted hydrogen being evolved while the metal enters into combination with the chlorous radicle of the acid. Nitric acid when concentrated decomposes most sulphides, with formation of metallic oxide, sulphuric acid, sulphur, and a lower oxide of nitrogen. Nitromuriatic acid acts in a similar manner, but still more energetically.

Sulphur-Salts.—The sulphides of the more basylous metals unite with those of the more chlorous or electro-negative metals, and of the non-metallic elements, forming sulphur-salts, analogous in composition to the oxygen-salts, *e. g.* :—



Selenides and Tellurides.—These compounds are analogous in composition, and in many of their properties, to the sulphides, and unite one with the other, forming selenium-salts and tellurium-salts analogous to the oxygen and sulphur salts.

Metals also form definite compounds with nitrogen, phosphorus, silicon, boron, and carbon: but these compounds are comparatively unimportant, excepting the carbonides of iron, which form cast-iron and steel.

CLASS I.—MONAD METALS.

GROUP I.—METALS OF THE ALKALIES.

POTASSIUM.

Atomic Weight, 39.1. Symbol, K (Kalium).

POTASSIUM was discovered in 1807 by Sir H. Davy, who obtained it in very small quantity by exposing a piece of moistened potassium hydroxide to the action of a powerful voltaic battery, the alkali being placed between a pair of platinum plates connected with the apparatus. Processes have since been devised for obtaining this metal in almost any quantity that can be desired.

An intimate mixture of potassium carbonate and charcoal is prepared by calcining, in a covered iron pot, the crude tartar of commerce; when cold it is rubbed to powder, mixed with one-tenth part of charcoal in small lumps, and quickly transferred to a retort of stout hammered iron: the latter may be one of the iron bottles in which mercury is imported. The retort is introduced into a furnace, *a* (fig. 147), and placed horizontally on supports of fire-brick, *f, f*. A wrought-iron tube, *d*, four inches long, serves to convey the vapors of potassium into a receiver, *e*, formed of two pieces of wrought-iron, *a, b* (fig. 148), which are fitted closely to each other,

Fig. 147.

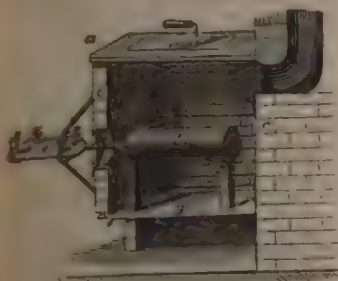
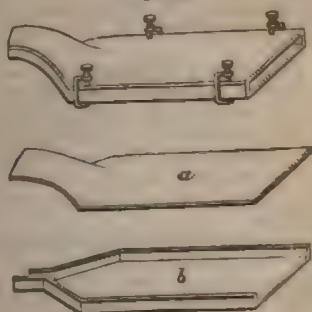


Fig. 148.



so as to form a shallow box only a quarter of an inch deep, and are kept together by clamp-screws. The iron plate should be one-sixth of an inch thick, twelve inches long, and five inches wide. The receiver is open at both ends, the socket fitting upon the neck of the iron bottle. The object of giving the receiver this flattened form is to insure the rapid cooling of the potassium, and thus to withdraw it from the action of the carbon monoxide, which is disengaged during the entire process, and has a strong tendency to unite with the potassium, forming a dangerously explosive compound. Before connecting the receiver with the tube *d*, the fire is slowly raised till the iron bottle attains a dull red heat. Powdered vitrified borax is then sprinkled upon it, which melts and forms a coating,

serving to protect the iron from oxidation. The heat is then to be urged until it is very intense, care being taken to raise it as equally as possible throughout every part of the furnace. When a full reddish-white heat is attained, vapors of potassium begin to appear, and burn with a bright flame. The receiver is then adjusted to the end of the tube, which must not project more than a quarter of an inch through the iron plate forming the front wall of the furnace; otherwise the tube is liable to be obstructed by the accumulation of solid potassium, or of the explosive compound above mentioned. Should any obstruction occur, it must be removed by thrusting in an iron bar, and, if this fail, the fire must be immediately withdrawn by removing the bars from the furnace, with the exception of two which support the iron bottle. The receiver is kept cool by the application of a wet cloth to its outside. When the operation is complete, the receiver with the potassium is removed and immediately plunged into a vessel of rectified petroleum, provided with a cover, and kept cool by immersion in water. When the apparatus is sufficiently cooled, the potassium is detached and preserved under petroleum.

If the potassium be wanted absolutely pure, it must be afterwards redistilled in an iron retort, into which some naphtha has been put, that its vapor may expel the air, and prevent oxidation of the metal.

Potassium is a brilliant white metal, with a high degree of lustre; at the common temperature of the air it is soft, and may be easily cut with a knife, but at 0°C . (32°F .) it is brittle and crystalline. It melts completely at 62.5°C . (144.5°F .), and distills at a low red heat. It floats on water, its specific gravity being only 0.865.

Exposed to the air, potassium oxidizes instantly, a tarnish covering the surface of the metal, which quickly thickens to a crust of caustic potash. Thrown upon water, it takes fire spontaneously, and burns with a beautiful purple flame, yielding an alkaline solution. When it is brought into contact with a little water in a jar standing over mercury, the liquid is decomposed with great energy, and hydrogen liberated. Potassium is always preserved under the surface of petroleum.

Potassium Chloride, KCl.—This salt is obtained in large quantity in the manufacture of the chlorate; it is easily purified from any portions of the latter by exposure to a dull red heat. Within the last few years, large quantities of this salt have been obtained from sea-water, by a peculiar process suggested by M. Balard.* It is also contained in kelp, and is separated for the use of the alum-maker. Considerable quantities of it are now obtained from the salt-beds of Stassfurt, near Magdeburg, in Prussia.

Potassium chloride closely resembles common salt in appearance, assuming, like that substance, the cubic form of crystallization. The crystals dissolve in three parts of cold, and in a much smaller quantity of boiling water: they are anhydrous, have a simple saline taste, with slight bitterness, and fuse when exposed to a red heat. Potassium chloride is volatilized by a very high temperature.

Potassium Iodide, KI.—There are three different methods of preparing this important medical compound.

(1) When iodine is added to a strong solution of caustic potash free from carbonate, it is dissolved in large quantity, forming a colorless solution containing potassium iodide and iodate; the reaction is the same as in the analogous case with chlorine. When the solution begins to be permanently colored by the iodine, it is evaporated to dryness, and cautiously

* Reports by the Juries of the International Exhibition of 1862, Class II.

heated to redness, by which the iodate is entirely converted into iodide. The mass is then dissolved in water, and, after filtration, made to crystallize.

(2) Iodine, water, and iron filings or scraps of zinc, are placed in a warm situation until the combination is complete, and the solution colorless. The resulting iodide of iron or zinc is then filtered, and exactly decomposed with solution of pure potassium carbonate, great care being taken to avoid excess of the latter. Potassium iodide and ferrous carbonate, or zinc carbonate, are thus obtained: the former is separated by filtration, and evaporated until the solution is sufficiently concentrated to crystallize on cooling, the washings of the filter being added to avoid loss:



(3) A very simple method for the preparation of potassium iodide was proposed by Liebig. One part of amorphous phosphorus is added to 40 parts of warm water; 20 parts of dry iodine are then gradually added and intimately mixed with the phosphorus by trituration. The dark-brown liquid thus obtained is now heated on the water-bath until it becomes colorless; it is then poured off from the undissolved phosphorus, and neutralized, first with barium carbonate and then with baryta-water, and it becomes slightly alkaline; and the insoluble barium phosphate is filtered off and washed. The filtrate now contains nothing but barium iodide, which, when treated with potassium sulphate, yields insoluble barium sulphate and potassium iodide in solution. Lime answers nearly as well as baryta.

Potassium iodide crystallizes in cubes, which are often, from some unexplained cause, milk-white and opaque: they are anhydrous, and fuse readily when heated. The salt is very soluble in water, but when pure, does not deliquesce in a moderately dry atmosphere: it is dissolved by alcohol.

Solution of potassium iodide, like those of all the soluble iodides, dissolves a large quantity of free iodine, forming a deep-brown liquid, not decomposed by water.

Potassium Bromide, KBr.—This compound may be obtained by processes exactly similar to those just described, substituting bromine for the iodine. It is a colorless and very soluble salt, quite undistinguishable in appearance and general characters from the iodine.

Potassium Oxides.—Potassium combines with oxygen in several proportions, forming a monoxide, K_2O , a dioxide, K_2O_2 , a tetroxide, K_2O_4 , and three oxides intermediate between the last two, besides a hydroxide, KHO , corresponding with the monoxide.

Potassium monoxide, K_2O , also called *anhydrous potash*, or *potassa*, is formed when potassium in thin slices is exposed at ordinary temperatures to dry air free from carbon dioxide; also when the hydroxide is heated with an equivalent quantity of metallic potassium:



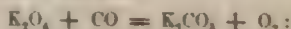
It is white, very deliquescent and caustic, combines energetically with water, forming potassium hydroxide, and becomes incandescent when moistened with it; melts at a red heat, and volatilizes at very high temperatures.

The dioxide, K_2O_2 , or $\begin{array}{c} \text{KO} \\ | \\ \text{KO} \end{array}$, is formed at a certain stage in the preparation of

the tetroxide, but has not been obtained quite pure. By carefully regulating the heat and supply of air, nearly the whole of the potassium may be converted into a white oxide, having nearly the composition of the dioxide. An aqueous solution of this oxide is formed by the action of water on the tetroxide.

The tetroxide, K_2O_4 , or $\begin{array}{c} K-O-O \\ | \\ K-O-O \end{array}$ is produced when potassium is burnt

in excess of dry air or oxygen gas. It is a chrome-yellow powder, which cakes together at about 280° . It absorbs moisture rapidly, and is decomposed by water, giving off oxygen, and forming a solution of the dioxide. When gently heated in a stream of carbon monoxide, it yields potassium carbonate and two atoms of oxygen:



with carbon dioxide it acts in a similar manner, giving off three atoms of oxygen.—Harcourt, *Chem. Soc. Journ.*, 1861, p. 267.

By passing dry air or nitrogen monoxide over potassium heated to a temperature below 100° , and stopping the action at certain stages, the oxides K_2O_2 , K_2O_3 , K_2O_4 , are obtained, intermediate between K_2O_2 and K_2O_4 .—(Lupton, *ibid.*, 1876, ii. 565.)

POTASSIUM HYDROXIDE, KHO , commonly called *caustic potash*, or *potassa*, is a very important substance, and one of great practical utility. It is always prepared by decomposing the carbonate with calcium hydroxide (slaked lime). 10 parts of potassium carbonate are dissolved in 100 parts of water, and heated to ebullition in a clean untinned iron, or, still better, silver vessel; 8 parts of good quicklime are meanwhile slaked in a covered basin, and the resulting calcium hydroxide is added, little by little, to the boiling solution of carbonate, with frequent stirring. When all the lime has been introduced, the mixture is suffered to boil for a few minutes, and then removed from the fire and covered up. In the course of a very short time, the solution will have become quite clear, and fit for decantation, the calcium carbonate, with the excess of hydrate, settling down as a heavy, sandy precipitate. The solution should not effervesce with acids.

It is essential in this process that the solution of potassium carbonate be dilute, otherwise the decomposition becomes imperfect. The proportion of lime recommended is much greater than that required by theory, but it is always proper to have an excess.

The solution of potassium hydroxide may be concentrated by quick evaporation in the iron or silver vessel to any desired extent; when heated until vapor of water ceases to be disengaged, and then suffered to cool, it furnishes the solid hydroxide, KHO or $K_2O.H_2O$.

Pure potassium hydroxide is also easily obtained by heating to redness for half an hour in a covered copper vessel, one part of pure powdered nitre with two or three parts of finely divided copper foil. The mass, when cold, is treated with water.

Potassium hydroxide is a white solid substance, very deliquescent, and soluble in water; alcohol also dissolves it freely, which is the case with comparatively few potassium compounds; the solid hydroxide of commerce, which is very impure, may thus be purified. The solution of this substance possesses, in the very highest degree, the properties termed alkaline: it restores the blue color to litmus which has been reddened by an acid; neutralizes completely the most powerful acids; has a nauseous and peculiar taste; and dissolves the skin, and many other organic matters, when the latter are subjected to its action. It is frequently used by surgeons as a caustery, being moulded into little sticks for that purpose.

Potassium hydroxide, both in the solid state and in solution, rapidly absorbs carbonic acid from the air: hence it must be kept in closely stopped bottles. When imperfectly prepared, or partially altered by exposure, it becomes white with an acid. It is not decomposed by heat, but volatilizes and is decomposed at a very high temperature.

The following table of the densities and value in anhydrous potassium oxide, K_2O , of different solutions of potassium hydroxide is given on the authority of Dalton:—

| Density. | Percentage of K_2O . | Density. | Percentage of K_2O . |
|------------|------------------------|------------|------------------------|
| 1.68 . . . | 51.2 | 1.33 . . . | 26.3 |
| 1.60 . . . | 46.7 | 1.28 . . . | 23.4 |
| 1.52 . . . | 42.9 | 1.23 . . . | 19.5 |
| 1.47 . . . | 39.6 | 1.19 . . . | 16.2 |
| 1.44 . . . | 36.8 | 1.15 . . . | 13.0 |
| 1.42 . . . | 34.4 | 1.11 . . . | 9.5 |
| 1.39 . . . | 32.4 | 1.06 . . . | 4.7 |
| 1.36 . . . | 29.4 | | |

Potassium Nitrate; Nitre; Saltpetre, $KNO_3 = NO_2(OK)$.—This important compound is a natural product, being disengaged by a kind of efflorescence from the surface of the soil in certain dry and hot countries. It may also be produced by artificial means, namely, by the oxidation of ammonia in presence of a powerful base.

In France, large quantities of artificial nitre are prepared by mixing animal refuse of all kinds with old mortar or slaked lime and earth, and placing the mixture in heaps, protected from the rain by a roof, but freely exposed to the air. From time to time the heaps are watered with putrid urine, and the mass is turned over, to expose fresh surfaces to the air. When much salt has been formed, the mixture is lixiviated, and the solution, which contains calcium nitrate, is mixed with potassium carbonate; calcium carbonate is formed, and the nitric acid transferred to the alkali. The filtered solution is then made to crystallize, and the crystals are purified by re-solution and crystallization, the liquid being stirred to prevent the formation of large crystals.

The greater part of the nitre used in this country comes from India: it is dissolved in water, a little potassium carbonate is added to precipitate lime, and then the salt is purified as above.

Considerable quantities of nitre are now manufactured by decomposing native sodium nitrate (Chile saltpetre) with carbonate or chloride of potassium. In Belgium the potassium carbonate obtained from the ashes of the bestroot sugar manufactories is largely used for this purpose; the potassium nitrate thus prepared is very pure, and is produced at a low price.

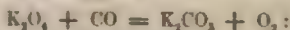
Potassium nitrate crystallizes in anhydrous six-sided prisms, with dihedral summits, belonging to the rhombic or trimetric system: it is soluble in 7 parts of water at $15.5^\circ C.$ ($60^\circ F.$), and in its own weight of boiling water. Its taste is saline and cooling, and it is without action on vegetable colors. It melts at a temperature below redness, and is completely decomposed by a strong heat.

When it is thrown on the surface of many metals in a state of fusion, or mixed with combustible matter and heated, rapid oxidation ensues, at the expense of the oxygen of the nitric acid. Examples of such mixtures are found in common gunpowder, and in nearly all pyrotechnic compositions, which burn in this manner independently of the oxygen of the air, and even under water. Gunpowder is made by very intimately mixing together potassium nitrate, charcoal, and sulphur, in proportions which approach 2 molecules of nitre, 3 atoms of carbon, and 1 atom of sulphur.

the tetroxide, but has not been obtained quite pure. By carefully regulating the heat and supply of air, nearly the whole of the potassium may be converted into a white oxide, having nearly the composition of the dioxide. An aqueous solution of this oxide is formed by the action of water on the tetroxide.

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with carbon dioxide it acts in a similar manner, giving off three atoms of oxygen.—Harcourt, *Chem. Soc. Journ.*, 1861, p. 267.

By passing dry air or nitrogen monoxide over potassium heated to a temperature below 100° , and stopping the action at certain stages, the oxides K_2O_3 , K_6O_4 , K_4O_3 , are obtained, intermediate between K_2O_3 and K_2O_4 .—(Lupton, *ibid.*, 1876, ii. 565.)

POTASSIUM HYDROXIDE, KHO , commonly called *caustic potash*, or *potassa*, is a very important substance, and one of great practical utility. It is always prepared by decomposing the carbonate with calcium hydroxide (slaked lime). 10 parts of potassium carbonate are dissolved in 100 parts of water, and heated to ebullition in a clean untinned iron, or, still better, silver vessel; 8 parts of good quicklime are meanwhile slaked in a covered basin, and the resulting calcium hydroxide is added, little by little, to the boiling solution of carbonate, with frequent stirring. When all the lime has been introduced, the mixture is suffered to boil for a few minutes, and then removed from the fire and covered up. In the course of a very short time, the solution will have become quite clear, and fit for decantation, the calcium carbonate, with the excess of hydrate, settling down as a heavy, sandy precipitate. The solution should not effervesce with acids.

It is essential in this process that the solution of potassium carbonate be dilute, otherwise the decomposition becomes imperfect. The proportion of lime recommended is much greater than that required by theory, but it is always proper to have an excess.

The solution of potassium hydroxide may be concentrated by quick evaporation in the iron or silver vessel to any desired extent; when heated until vapor of water ceases to be disengaged, and then suffered to cool, it furnishes the solid hydroxide, KHO or $K_2O.H_2O$.

Pure potassium hydroxide is also easily obtained by heating to redness for half an hour in a covered copper vessel, one part of pure powdered nitre with two or three parts of finely divided copper foil. The mass, when cold, is treated with water.

Potassium hydroxide is a white solid substance, very deliquescent, and soluble in water; alcohol also dissolves it freely, which is the case with comparatively few potassium compounds; the solid hydroxide of commerce, which is very impure, may thus be purified. The solution of this substance possesses, in the very highest degree, the properties termed alkaline: it restores the blue color to litmus which has been reddened by an acid; neutralizes completely the most powerful acids; has a nauseous and peculiar taste; and dissolves the skin, and many other organic matters, when the latter are subjected to its action. It is frequently used by surgeons as a *cautery*, being moulded into little sticks for that purpose.

Potassium hydroxide, both in the solid state and in solution, rapidly absorbs carbonic acid from the air: hence it must be kept in closely stopped bottles. When imperfectly prepared, or partially altered by exposure, it effervesces with an acid. It is not decomposed by heat, but volatilizes undecomposed at a very high temperature.

The following table of the densities and value in anhydrous potassium oxide, K_2O , of different solutions of potassium hydroxide is given on the authority of Dalton:—

| Density. | Percentage of K_2O . | Density. | Percentage of K_2O . |
|------------|------------------------|------------|------------------------|
| 1.68 . . . | 51.2 | 1.33 . . . | 26.3 |
| 1.60 . . . | 46.7 | 1.28 . . . | 23.4 |
| 1.52 . . . | 42.9 | 1.23 . . . | 19.5 |
| 1.47 . . . | 39.6 | 1.19 . . . | 16.2 |
| 1.44 . . . | 36.8 | 1.15 . . . | 13.0 |
| 1.42 . . . | 34.4 | 1.11 . . . | 9.5 |
| 1.39 . . . | 32.4 | 1.06 . . . | 4.7 |
| 1.36 . . . | 29.4 | | |

Potassium Nitrate; Nitre; Saltpetre, $KNO_3 = NO_2(OK)$.—This important compound is a natural product, being disengaged by a kind of effluence from the surface of the soil in certain dry and hot countries. It may also be produced by artificial means, namely, by the oxidation of ammonia in presence of a powerful base.

In France, large quantities of artificial nitre are prepared by mixing animal refuse of all kinds with old mortar or slaked lime and earth, and placing the mixture in heaps, protected from the rain by a roof, but freely exposed to the air. From time to time the heaps are watered with putrid urine, and the mass is turned over, to expose fresh surfaces to the air. When much salt has been formed, the mixture is lixiviated, and the solution, which contains calcium nitrate, is mixed with potassium carbonate; calcium carbonate is formed, and the nitric acid transferred to the alkali. The filtered solution is then made to crystallize, and the crystals are purified by re-solution and crystallization, the liquid being stirred to prevent the formation of large crystals.

The greater part of the nitre used in this country comes from India; it is dissolved in water, a little potassium carbonate is added to precipitate lime, and then the salt is purified as above.

Considerable quantities of nitre are now manufactured by decomposing native sodium nitrate (Chile saltpetre) with carbonate or chloride of potassium. In Belgium the potassium carbonate obtained from the ashes of the beetroot sugar manufactories is largely used for this purpose; the potassium nitrate thus prepared is very pure, and is produced at a low price.

Potassium nitrate crystallizes in anhydrous six-sided prisms, with di-hedral summits, belonging to the rhombic or trimetric system: it is soluble in 7 parts of water at $15.5^\circ C.$ ($60^\circ F.$), and in its own weight of boiling water. Its taste is saline and cooling, and it is without action on vegetable colors. It melts at a temperature below redness, and is completely decomposed by a strong heat.

When it is thrown on the surface of many metals in a state of fusion, or mixed with combustible matter and heated, rapid oxidation ensues, at the expense of the oxygen of the nitric acid. Examples of such mixtures are found in common gunpowder, and in nearly all pyrotechnic compositions, which burn in this manner independently of the oxygen of the air, and even under water. Gunpowder is made by very intimately mixing together potassium nitrate, charcoal, and sulphur, in proportions which approach 2 molecules of nitre, 3 atoms of carbon, and 1 atom of sulphur.

These quantities give, reckoned to 100 parts, and compared with the proportions used in the manufacture of the English Government powder, the following results :—

| | Theory. | Proportions
in practice. |
|-----------------------------|-------------|-----------------------------|
| Potassium nitrate | 74.8 | 75 |
| Charcoal | 13.3 | 15 |
| Sulphur | 11.9 | 10 |
| | <hr/> 100.0 | <hr/> 100 |

The nitre is rendered very pure by the means already mentioned, freed from water by fusion, and ground to fine powder; the sulphur and charcoal, the latter being made from light wood, as dogwood or alder, are also finely ground, after which the materials are weighed out, moistened with water, and thoroughly mixed by grinding under an edge-mill. The mass is then subjected to great pressure, and the mill-cake thus produced broken in pieces, and placed in sieves made of perforated vellum, moved by machinery, each containing, in addition, a round piece of heavy wood. The grains of powder broken off by attrition fall through the holes in the skin, and are easily separated from the dust by sifting. The powder is, lastly, dried by exposure to steam-heat, and sometimes glazed or polished by agitation in a kind of cask mounted on an axis.

It was formerly supposed that when gunpowder is fired, the whole of the oxygen of the potassium nitrate was transferred to the carbon, forming carbon dioxide, the sulphur combining with the potassium, and the nitrogen being set free. There is no doubt that this reaction does take place to a considerable extent, and that the large volume of gas thus produced, and still further expanded by the very high temperature, sufficiently accounts for the explosive effects. But recent investigations by Bunsen, Karolyi, and others, have shown that the actual products of the combustion of gunpowder are much more complicated than this theory would indicate, a very large number of products being formed, and a considerable portion of the oxygen being transferred to the potassium sulphide, converting it into sulphate, which, in fact, constitutes the chief portion of the solid residue and of the smoke formed by the explosion.*

Potassium Chlorate, $\text{KClO}_3 = \text{ClO}_2(\text{OK})$.—The theory of the production of chloric acid by the action of chlorine gas on a solution of caustic potash, has been already explained (p. 183). Chlorine gas is conducted by a wide tube into a strong and warm solution of potassium carbonate, until absorption of the gas ceases; and the liquid is, if necessary, evaporated, and then left to cool, in order that the slightly soluble chlorate may crystallize out. The mother-liquor affords a second crop of crystals, but they are much more contaminated with potassium chloride. It may be purified by one or two re-crystallizations.

Potassium chlorate is soluble in about 20 parts of cold and 2 of boiling water: the crystals are anhydrous, flat, and tabular; in taste it somewhat resembles nitre. When heated it gives off the whole of its oxygen as gas and leaves potassium chloride. By arresting the decomposition when the evolution of gas begins to slacken, and redissolving the salt, potassium perchlorate and chloride may be obtained.

This salt deflagrates violently with combustible matter, explosion often occurring by friction or blows. When about one grain-weight of chlorate and an equal quantity of sulphur are rubbed in a mortar, the mixture ex-

* See Watts's Dictionary of Chemistry, vol. ii. p. 268.

plodes with a loud report; hence it cannot be used in the preparation of gunpowder instead of the nitrate. Potassium chlorate is now a large article of commerce, being employed, together with phosphorus, in making instantaneous-light matches.

Potassium Perchlorate, $\text{KClO}_4 = \text{ClO}_2(\text{OK})$.—This salt has been already noticed under the head of perchloric acid. It is best prepared by projecting powdered potassium chlorate into warm nitric acid, when the chloric acid is resolved into perchloric acid, chlorine and oxygen. The salt is separated from the nitrate by crystallization. Potassium perchlorate is a very slightly soluble salt: it requires 55 parts of cold water, but is more freely taken up at a boiling heat. The crystals are small, and have the figure of an octohedron with square base. It is decomposed by heat in the same manner as the chlorate.

Potassium Carbonates.—Potassium forms two well-defined carbonates, namely, a normal or neutral carbonate, K_2CO_3 , and an acid salt containing KHCO_3 .

Normal potassium carbonate, or Dipotassic carbonate, $\text{K}_2\text{CO}_3 = \text{CO}(\text{OK})_2 = \text{K}_2\text{O.C.O}_2$.—Potassium salts of vegetable acids are of constant occurrence in plants, in the economy of which they perform important, but not yet perfectly understood functions. The potassium is derived from the soil, which, when capable of supporting vegetable life, always contains that substance. When plants are burned, the organic acids are destroyed, and the potassium is left in the state of carbonate.

It is by these indirect means that the carbonate, and thence nearly all the salts of potassium, are obtained. The great natural depository of the alkalis is the felspar of granitic and other unstratified rocks, where it is combined with silica, and in an insoluble state. The extraction thence is attended with great difficulties, and many attempts at manufacturing it on a large scale from this source have failed; but experiments recently made by Mr. T. O. Ward appear to indicate that the object may be accomplished by fusing potassic rocks with a mixture of calcium carbonate and fluoride. There are, however, natural processes at work, by which the potash is constantly being eliminated from these rocks. Under the influence of atmospheric agencies, these rocks disintegrate into soils, and as the alkali acquires solubility, it is gradually taken up by plants, and accumulates in their substance in a condition highly favorable to its subsequent applications.

Potassium-salts are always most abundant in the green and tender parts of plants, as may be expected, since from these, evaporation of nearly pure water takes place to a large extent: the solid timber of forest trees contains comparatively little.

In preparing the salt on an extensive scale, the ashes are subjected to a process called *lixivation*: they are put into a large cask or tun, having, near the bottom, an aperture stopped by a plug, and a quantity of water is added. After some hours the liquid is drawn off, and more water added, that the whole of the soluble matter may be removed. The weakest solutions are poured upon fresh quantities of ash, in place of water. The solutions are then evaporated to dryness, and the residue is burned, to remove a little brown organic matter: the product is the crude potash or pearl ash of commerce, of which very large quantities are obtained from Russia and America. The salt is very impure: it contains potassium silicate, sulphate, chloride, etc.

The purified potassium carbonate of pharmacy is prepared from the crude article by adding an equal weight of cold water, agitating and filtering; most of the foreign salts are, from their inferior degree of solu-

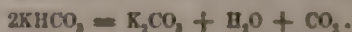
bility, left behind. The solution is then boiled down to a very small bulk, and left to cool, when the carbonate separates in small crystals containing 2 molecules of water, $K_2CO_3 \cdot 2H_2O$; these are drained from the mother-liquor, and then dried in a stove.

A still purer salt may be obtained by exposing to a red heat purified cream of tartar (acid potassium tartrate), and separating the carbonate by solution in water and crystallization, or evaporation to dryness.

Potassium carbonate is extremely deliquescent, and soluble in less than its own weight of water: the solution is highly alkaline to test-paper. It is insoluble in alcohol. By heat the water of crystallization is driven off, and by a temperature of full ignition the salt is fused, but not otherwise changed. This substance is largely used in the arts, and is a compound of great importance.

Acid potassium carbonate, Hydrogen and potassium carbonate, or Monopotassic carbonate, $KHCO_3$; commonly called *bicarbonate of potash*.—When a stream of carbonic acid gas is passed through a cold solution of potassium carbonate, the gas is rapidly absorbed, and a white, crystalline, less soluble substance separated, which is the acid salt. It is collected, pressed, re-dissolved in warm water, and the solution is left to crystallize.

Acid potassium carbonate is much less soluble than the normal carbonate, requiring 4 parts of cold water to dissolve it. The solution is nearly neutral to test-paper, and has a much milder taste than the normal salt. When boiled it gives off carbon dioxide. The crystals, which are large and beautiful, derive their form from a monoclinic prism: they are decomposed by heat, water and carbon dioxide being evolved, and normal carbonate left behind:—



Potassium Sulphates.—Potassium forms a normal or neutral sulphate, two acid sulphates, and an anhydrosulphate.

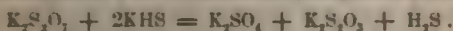
Normal potassium sulphate, or Dipotassic sulphate, $K_2SO_4 = SO_4(OK)_2 = K_2O \cdot SO_3$, is obtained by neutralizing the acid residue left in the retort when nitric acid is prepared, with crude potassium carbonate. The solution yields, on cooling, hard, transparent crystals of the neutral sulphate, which may be re-dissolved in boiling water, and re-crystallized.

Potassium sulphate is soluble in about 10 parts of cold, and in a much smaller quantity of boiling water: it has a bitter taste, and is neutral to test-paper. The crystals are combinations of rhombic pyramids and prisms, much resembling those of quartz in figure and appearance: they are anhydrous, and decrepitate when suddenly heated, which is often the case with salts containing no water of crystallization. They are quite insoluble in alcohol.

Acid potassium sulphate, Hydrogen and potassium sulphate, or Monopotassic sulphate, $KHSO_4 = SO_4(OK)(OH)$, commonly called *bisulphate of potash*.—To obtain this salt the neutral sulphate in powder is mixed with half its weight of oil of vitriol, and the whole evaporated quite to dryness in a platinum vessel placed under a chimney: the fused salt is dissolved in hot water and left to crystallize. The crystals have the figure of flattened rhombic prisms, and are much more soluble than the neutral salt, requiring only twice their weight of water at $15.50^\circ C.$ ($600^\circ F.$), and less than half that quantity at $100^\circ C.$ ($212^\circ F.$). The solution has a sour taste and strongly acid reaction.

Potassium Disulphate, or Pyrosulphate, $K_2S_2O_7$, derived from Nordhausen sulphuric acid, $H_2S_2O_7$, and commonly called *anhydrous bisulphate of potash*, is obtained by dissolving equal weights of the normal sulphate and oil of vitriol in a small quantity of warm distilled water, and leaving the solution to cool.

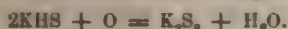
The pyro-sulphate crystallizes out in long delicate needles, which if left for several days in the mother-liquor disappear, and give place to crystals of the ordinary acid sulphate above described. This salt is decomposed by a large quantity of water, and is converted by strong fuming sulphuric acid into *hydropotassic pyrosulphate*, KHS_2O_7 , which crystallizes in transparent prisms. The neutral pyrosulphate in fine powder, heated with an alcoholic solution of potassium hydrosulphide, is converted into sulphate and thiosulphate, with evolution of hydrogen sulphide:—



Potassium Sulphides.—Potassium heated in sulphur vapor burns with great brilliancy. It unites with sulphur in five different proportions, forming the compounds K_2S , K_2S_2 , K_2S_3 , K_2S_4 , K_2S_5 ; also a hydrosulphide or sulphhydrate, KHS .

Monosulphide, K_2S .—It is doubtful whether this compound has been obtained in the pure state. It is commonly said to be produced by heating potassium sulphate in a current of dry hydrogen, or by igniting the same salt in a covered vessel with finely-divided charcoal; but, according to Bauer, one of the higher sulphides is always formed at the same time, together with oxide of potassium. The product has a reddish-yellow color, is deliquescent, and acts as a caustic on the skin. When potassium sulphate is heated in a covered crucible with excess of lamp-black, a mixture of potassium sulphide and finely-divided carbon is obtained, which takes fire spontaneously on coming in contact with the air. The monosulphide might perhaps be obtained pure by heating 1 molecule of potassium sulphhydrate, KHS , with 1 atom of the metal.

When sulphydric acid gas is passed to saturation into a solution of caustic potash, a solution of the sulphhydrate is obtained, which is colorless at first, but, if exposed to the air, quickly absorbs oxygen, and turns yellow, in consequence of the formation of bisulphide:—



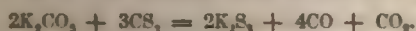
If a solution of potash be divided into two parts, one-half saturated with hydrogen sulphide, and then mixed with the other, a solution is formed which may contain potassium monesulphide:—



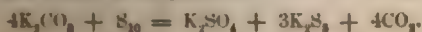
But it is also possible that the hydroxide and hydrosulphide may mix without mutual decomposition. The solution, when mixed with one of the stronger acids, gives off hydrogen sulphide without deposition of sulphur, a reaction which is consistent with either view of its constitution.

The **bisulphide, K_2S_2** , is formed, as already observed, on exposing a solution of the hydrosulphide to the air till it begins to show turbidity. By evaporation in a vacuum, it is obtained as an orange-colored, easily fusible substance.

The **trisulphide, K_2S_3** , is obtained by passing the vapor of carbon bisulphide over ignited potassium carbonate, as long as gas continues to escape:—



Also, together with potassium sulphate, forming one of the mixtures called *brer of sulphur*, by melting 352 parts (4 molecules) of potassium carbonate with 320 parts (10 atoms) of sulphur:—

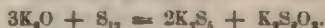


The *tetrasulphide*, K_2S_4 , is formed by reducing potassium sulphate with the vapor of carbon bisulphide.

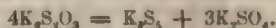
The *pentasulphide*, K_2S_5 , is formed by boiling a solution of any of the preceding sulphides with excess of sulphur till it is saturated, or by fusing either of them in the dry state with sulphur. The excess of sulphur then separates and floats above the dark-brown pentasulphide.

Liver of sulphur, or *hepar sulphuris*, is a name given to a brownish substance, sometimes used in medicine, made by fusing together different proportions of potassium carbonate and sulphur. It is a variable mixture of the two higher sulphides with thiosulphate and sulphate of potassium.

When equal parts of sulphur and dry potassium carbonate are melted together at a temperature not exceeding $250^\circ C.$ ($482^\circ F.$), the decomposition of the salt is quite complete, and all the carbon dioxide is expelled. The fused mass dissolves in water, with the exception of a little mechanically mixed sulphur, with dark-brown color, and the solution is found to contain nothing besides pentasulphide and thiosulphate of potassium:—



When the mixture has been exposed to a temperature approaching that of ignition, it is found, on the contrary, to contain potassium sulphate, arising from the decomposition of the thiosulphate which then occurs:—



From both these mixtures the potassium pentasulphide may be extracted by alcohol, in which it dissolves.

When the carbonate is fused with half its weight of sulphate only, the trisulphide is produced, as above indicated, instead of the pentasulphide.

The effects described happen in the same manner when potassium hydroxide is substituted for the carbonate; also, when a solution of the hydroxide is boiled with sulphur, a mixture of sulphide and thiosulphate always results.

Potassium salts are colorless when not associated with a colored metallic oxide or acid. They are all more or less soluble in water, and may be distinguished by the following characters:—

(1) Solution of *tartaric acid*, added in excess to a moderately strong solution of a potassium-salt, gives, after some time, a white crystalline precipitate of cream of tartar; the effect is greatly promoted by strong agitation.

(2) Solution of *platinic chloride*, with a little hydrochloric acid, if necessary, gives, under similar circumstances, a crystalline yellow precipitate, which is a double salt of platinum tetrachloride and potassium chloride. Both this compound and cream of tartar are, however, soluble in about 60 parts of cold water. An addition of alcohol increases the delicacy of both tests.

(3) *Perchloric acid*, and *silicofluoric acid*, give rise to slightly soluble white precipitates when added to a potassium-salt.

(4) Potassium salts usually color the outer blow-pipe flame purple or violet; this reaction is clearly perceptible only when the potassium-salts are pure.

(5) The spectral phenomena exhibited by potassium compounds are mentioned at page 87.

SODIUM.

Atomic weight, 23. Symbol, Na (Natrium).

Sodium is a very abundant element, and very widely diffused. It occurs in large quantities as chloride, in rock-salt, sea-water, salt-springs, and many other mineral waters; more rarely as carbonate, borate, and sulphate, in solution or in the solid state, and as silicate in many minerals.

Metallic sodium was obtained by Davy soon after the discovery of potassium, and by a similar means. Gay-Lussac and Thénard afterwards prepared it by decomposing sodium hydroxide with metallic iron at a white heat, and Brunner showed that it may be prepared with much greater facility by distilling a mixture of sodium carbonate and charcoal.

The preparation of sodium by this last-mentioned process is much easier than that of potassium, not being complicated, or only to a slight extent, by the formation of secondary products. Within the last few years it has been considerably improved by Deville and others, and carried out on the manufacturing scale, sodium being now employed in considerable quantity as a reducing agent, especially in the manufacture of aluminium and magnesium, and in the silver amalgamation process.

The sodium carbonate used for the preparation is prepared by calcining the crystallized neutral carbonate. It must be thoroughly dried, then pounded, and mixed with a slight excess of pounded charcoal or coal. An inactive substance, viz., pounded chalk, is also added to keep the mixture in a pasty condition during the operation, and prevent the fused sodium carbonate from separating from the charcoal. The following are the proportions recommended by Deville:—

| <i>For Laboratory Operations.</i> | | <i>For Manufacturing Operations.</i> | |
|-----------------------------------|--------------|--------------------------------------|--------------|
| Dry sodium carbonate | . 717 parts. | Dry sodium carbonate | . 30 kilogr. |
| Charcoal | . . . 175 " | Coal | . . . 13 " |
| Chalk | . . . 108 " | Chalk | . . . 3 " |

These materials must be very intimately mixed by pounding and sifting, and it is advantageous to calcine the mixture before introducing it into the distilling apparatus, provided the calcination can be effected by the waste heat of a furnace; the mixture is thereby rendered more compact, so that a much larger quantity can be introduced into a vessel of given size.

The distillation is performed, on the laboratory scale, in a mercury bottle heated exactly in the manner described for the preparation of potassium. For manufacturing operations, the mixture is introduced into iron cylinders, which are heated in a reverberatory furnace, and so arranged that, at the end of the distillation, the exhausted charge may be withdrawn and a fresh charge introduced, without displacing the cylinders or putting out the fire. The receivers used in either case are the same in form and dimensions as those employed in the preparation of potassium (p. 293).

When the process goes on well, the sodium collected in the receivers is nearly pure; it may be completely purified by melting it under a thin layer of petroleum. This liquid is decanted as soon as the sodium becomes perfectly fluid, and the metal is run into moulds like those used for casting lead or zinc.

Sodium is a silver-white metal, greatly resembling potassium in every

respect. Its specific gravity is 0.972. It is soft at common temperatures, melts at 97.6°C . (207.7°F .), and oxidizes very rapidly in the air. When placed on the surface of cold water, it decomposes that liquid with great violence, but seldom takes fire unless the motions of the fragment are restrained, and its rapid cooling is diminished by adding gum or starch to the water. With hot water it takes fire at once, burning with a bright yellow flame, and producing a solution of soda.

Sodium Chloride; Common Salt, NaCl .—This very important substance is found in many parts of the world in solid beds or irregular strata of immense thickness, as in Cheshire, Spain, Galicia, and many other localities. An inexhaustible supply exists also in the waters of the ocean, and large quantities are obtained from saline springs.

Rock-salt is almost always too impure for use. If no natural brine-spring exists, an artificial one is formed by sinking a shaft into the rock-salt, and, if necessary, introducing water. This when saturated is pumped up, and evaporated more or less rapidly in large iron pans. As the salt separates, it is removed from the bottom of the vessel by means of a scoop, pressed while still moist into moulds, and then transferred to the drying-stove. When large crystals are required, as for the coarse-grained *bay-salt* used in curing provisions, the evaporation is slowly conducted. Common salt is apt to be contaminated with magnesium chloride.

Sodium chloride, when pure, is not deliquescent in moderately dry air. It crystallizes in anhydrous cubes, which are often grouped together into pyramids, or steps. It requires about $2\frac{1}{2}$ parts of water at 60°F . for solution, and its solubility is not sensibly increased by heat; it dissolves to some extent in spirit of wine, but is nearly insoluble in absolute alcohol. It melts at a red heat, and is volatile at a still higher temperature. The economical uses of common salt are well known.

The *iodide and bromide of sodium* much resemble the corresponding potassium compounds: they crystallize in cubes, which are anhydrous, and very soluble in water.

Sodium Oxides.—Sodium forms a monoxide and a dioxide; also a hydroxide corresponding with the former.

Sodium Monoxide, or Anhydrous Soda, Na_2O . is produced, together with the dioxide, when sodium burns in the air, and may be obtained pure by exposing the dioxide to a very high temperature; or by heating sodium hydroxide with an equivalent quantity of sodium: $2\text{NaHO} + \text{Na} = 2\text{Na}_2\text{O} + \text{H}_2$. It is a gray mass, which melts at a red heat, and volatilizes with difficulty.

Sodium Hydroxide, or Caustic Soda, NaHO , or $\text{Na}_2\text{O} \cdot \text{H}_2\text{O}$.—This substance is prepared by decomposing a somewhat dilute solution of sodium carbonate with calcium hydroxide: the description of the process employed in the case of potassium hydroxide, and the precautions necessary, apply word for word to that of sodium hydroxide.

The solid hydroxide is a white fusible substance, very similar in properties to potassium hydroxide. It is deliquescent, but dries up again after a time in consequence of the absorption of carbonic acid. The solution is highly alkaline, and a powerful solvent for animal matter: it is used in large quantity for making soap.

The strength of a solution of caustic soda may be roughly determined from a knowledge of its density, by the aid of the following table drawn up by Dalton:—

TABLE OF PERCENTAGES OF ANHYDROUS SODA, Na_2O , IN SOLUTIONS OF DIFFERENT DENSITY.

| Density. | Percentage of anhydrous soda. | Density. | Percentage of anhydrous soda. |
|------------|-------------------------------|------------|-------------------------------|
| 2.00 . . . | 77.8 | 1.40 . . . | 29.0 |
| 1.85 . . . | 63.6 | 1.36 . . . | 26.0 |
| 1.72 . . . | 53.8 | 1.32 . . . | 23.0 |
| 1.63 . . . | 46.6 | 1.29 . . . | 19.0 |
| 1.56 . . . | 41.2 | 1.23 . . . | 16.0 |
| 1.50 . . . | 36.8 | 1.18 . . . | 13.0 |
| 1.47 . . . | 34.0 | 1.12 . . . | 9.0 |
| 1.44 . . . | 31.0 | 1.06 . . . | 4.7 |

Sodium Dioxide, Na_2O_2 .—Sodium, when heated to about 2000°C . (3620°F) in a current of dry air, absorbs oxygen, and is converted into dioxide; the substance is white, but becomes yellow when heated, which tint it again loses on cooling. It dissolves in water without decomposition: the solution may be evaporated under the receiver of the air-pump, and, when sufficiently concentrated, deposits crystalline plates having the composition $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. These crystals, left to effloresce over oil of vitriol for nine days, lose three-fourths of their water, and yield another hydrate containing $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. The aqueous solution of sodium dioxide when heated on the water-bath, is decomposed into oxygen and the monoxide.

Sodium Nitrate, NaNO_3 .—This salt, sometimes called *Cubic nitre*, or *Chile saltpetre*, occurs native, and in enormous quantity, at Tarapaca, in Northern Peru, where it forms a regular bed, of great extent, along with gypsum, common salt, and remains of recent shells. The pure salt commonly crystallizes in rhombohedrons, resembling those of calcareous spar. It is deliquescent, and very soluble in water. Sodium nitrate is employed for making nitric acid, but cannot be used for gunpowder, as the mixture burns too slowly, and becomes damp in the air. It has been lately used with some success in agriculture as a superficial manure or top-dressing; also, for preparing potassium nitrate (p. 297).

Sodium Carbonates.—The *Neutral* or *Disodic Carbonate*, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, was once exclusively obtained from the ashes of sea-weeds, and of plants, such as the *Salsola soda*, which grow by the seaside, or, being cultivated in suitable localities for the purpose, are afterwards subjected to incineration. The *barilla*, still employed to a small extent in soap-making, is thus produced in several places on the coast of Spain, as at Alicante, Carthage, &c. That made in Brittany is called *verre*.

Sodium carbonate is now manufactured on a stupendous scale from common salt by a series of processes which may be divided into two stages:—

(1) Manufacture of sodium sulphate, or salt-cake, from sodium chloride (common salt); this is called the salt-cake process.

(2) Manufacture of sodium carbonate, or soda-ash; called the soda-ash process.

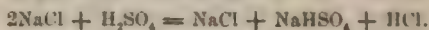
(1) *Salt-cake process.*—This process consists in the decomposition of common salt by sulphuric acid, and is effected in a furnace called the *Salt-cake furnace*, of which fig. 149 represents a section. It consists of a large covered iron pan, placed in the centre, and heated by a fire underneath; and two roasters, or reverberatory furnaces, placed one at each end, and on the hearths of which the salt is completely decomposed. The charge of half a ton of salt is first placed in the iron pan, and then the requisite quantity of sulphuric acid is allowed to pass in upon it. Hydrochloric

acid is evolved, and escapes through a flue, with the products of combustion, into towers or scrubbers, filled with coke and bricks moistened with a stream of water; the acid vapors are thus condensed, and the smoke and heated air pass up the chimney. After the mixture of salt and acid

Fig. 140.



has been heated in the iron pan, it becomes converted into a solid mass of acid sodium sulphate and undecomposed sodium chloride:—

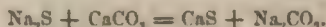


It is then raked on to the hearths of the furnaces at each side of the decomposing pan, where the flame and heated air of the fire complete the decomposition into neutral sodium sulphate and hydrochloric acid:—



(2) *Soda-ash process.*—The sulphate is next reduced to powder, and mixed with an equal weight of chalk or limestone, and half as much small coal, both ground or crushed. The mixture is thrown into a reverberatory furnace, and heated to fusion, with constant stirring. When the decomposition is judged complete, the melted matter is raked from the furnace into an iron trough, where it is allowed to cool. This crude product, called *black ash* or *ball-soda*, is broken up into little pieces, when cold, and lixiviated with cold or tepid water. The solution is evaporated to dryness, and the salt calcined with a little sawdust in a suitable furnace. The product is the *soda ash* or *British alkali* of commerce, which, when of good quality, contains from 48 to 52 per cent. of anhydrous soda, Na_2O , partly in the state of carbonate, and partly as hydroxide, the remainder being chiefly sodium sulphate and common salt, with occasional traces of sulphite or thiosulphate, and also cyanide of sodium. By dissolving soda-ash in hot water, filtering the solution, and then allowing it to cool slowly, the carbonate is deposited in large transparent crystals.

The reaction which takes place in the calcination of the sulphate with chalk and coal-dust seems to consist, first, in the conversion of the sodium sulphate into sulphide by the aid of the combustible matter, and, secondly, in the interchange of elements between that substance and the calcium carbonate:—



Several other processes for the manufacture of soda have been devised and even carried into execution, but the only one which appears to hold out any prospect of commercial success is that which is called the “*ammonia soda-process*.”* This method, first suggested about forty years ago, has been tried at several works in England and in Germany. It consists in decomposing a solution of common salt with ammonium bicarbonate, whereby the greater part of the sodium is precipitated as bicarbonate, while the ammonia remains in solution as ammonium chloride. This lat-

* *Chemisches Centralblatt*, 1873, p. 630; 1874, pp. 274, 370, 502.

ter salt is heated with lime to liberate ammonia, which is then reconverted into bicarbonate by the carbonic acid evolved in the conversion of the sodium bicarbonate into monocarbonate by heat; and the ammonium bicarbonate thus reproduced is employed to decompose fresh portions of sodium chloride, so that the process is made continuous. The chief advantages claimed for this process are the direct conversion of the sodium chloride into carbonate, which is precipitated from the concentrated liquors uncontaminated with salts of other metals; the absolute freedom of the product from sulphur-compounds; and lastly, simplicity of plant, saving of fuel, and freedom from noxious vapors and troublesome secondary products.

The chief obstacle to its profitable employment appears to be that, with certain proportions of the materials, and under certain conditions of temperature and concentration, a reverse reaction takes place, whereby the sodium bicarbonate and ammonium chloride are reconverted into ammonium carbonate and sodium chloride.

The ordinary crystals of sodium carbonate contain ten molecules of water; but by particular management the same salt may be obtained with fifteen, nine, seven molecules, or sometimes with only one. The common form of the crystals is derived from an oblique rhombic prism; they effloresce in dry air, and crumble to a white powder. Heated, they fuse in their water of crystallization; when the latter has been expelled, and the dry salt exposed to a full red heat, it melts without undergoing change. The common crystals dissolve in two parts of cold, and in less than their own weight of boiling water: the solution has a strong, disagreeable, alkaline taste, and a powerfully alkaline reaction.

Hydrogen and Sodium Carbonate, Hydrosodic Carbonate, Monosodic Carbonate, Acid Sodium Carbonate, NaHCO_3 or $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{CO}_3$, commonly called *Bicarbonate of soda*.—This salt is prepared by passing carbonic acid gas into a concentrated solution of the neutral carbonate, or by placing the crystals in an atmosphere of the gas, which is rapidly absorbed, while the crystals lose the greater part of their water, and pass into the new compound.

Monosodic carbonate, prepared by either process, is a crystalline white powder, which cannot be redissolved in warm water without partial decomposition. It requires 10 parts of water at 15.5°C for solution: the liquid is feebly alkaline to test-paper, and has a much milder taste than that of the neutral carbonate. It does not precipitate a solution of magnesium. By exposure to heat, the salt is converted into neutral carbonate.

Decahydro-tetrasodic Carbonate, $\text{Na}_4\text{H}_4(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$.—This salt, commonly called *sequecarbonate of soda*, may be regarded as a compound of the neutral and acid salts ($\text{Na}_2\text{CO}_3 \cdot 2\text{NaHCO}_3$). It occurs native on the banks of the soda lakes of Sokenna, near Fezzan, in Africa, where it is called *trouai*; also *de anas*, at the bottom of a lake in Maracaibo, South America. It is produced artificially, though with some difficulty, by mixing the monosodic and tetrasodic carbonates in the proportions above indicated, melting them together, drying, and exposing the dried mass in a cellar for some weeks; it then absorbs water, becomes crystalline, and contains spaces filled with the tetrasodic carbonate.

Sodium and Potassium Carbonate, $\text{NaKCO}_3 \cdot 6\text{H}_2\text{O}$, separates in monoclinic crystals from a solution containing the two carbonates in equivalent proportions.

A mixture of these two carbonates in equivalent proportions melts at a much lower heat than either of the salts separately; such a mixture is very useful in the fusion of silicates, etc.

Alkalimetry.—Analysis of Alkaline Hydroxides and Carbonates.

The amount of alkali or alkaline carbonate in commercial potash soda, or ammonia, is estimated by determining the quantity of an acid of given

strength required to neutralize a given weight of the sample. The estimation depends upon the facts that the alkaline salts of strong acids (sulphuric, oxalic, etc.) are neutral to litmus : and that the violet solution of litmus is colored blue by caustic alkalis or alkaline carbonates, wine-red by carbonic acid, and light red by strong acids.

The first step is the preparation of the standard acid. It is best to make this liquid of such strength that 1000 cubic centimetres (1 litre) shall contain exactly one $\frac{1}{2}$ gram-molecule (*i. e.*, 1 molecule expressed in $\frac{1}{2}$ grams) of the acid.

About 70 grams of concentrated sulphuric acid are diluted with about 600 grams of water ; when the mixture is cool, the volume of it necessary to saturate 5.3 grams (one $\frac{1}{2}$ decigram-molecule) of pure anhydrous sodium carbonate, Na_2CO_3 , is determined.* For this purpose 5.3 grams of freshly ignited sodium carbonate are dissolved in hot water, the solution colored blue with a few drops of litmus, and the acid added from a burette or alkalimetre (p. 309), at last drop by drop, till the color just passes from wine-red to light red, and till strips of litmus-paper, moistened with the solution, begin to retain the color when dry. The volume of acid employed is then noted, and the whole diluted so as to approximate to the required strength. Suppose, for instance, 37 cubic centimetres of acid have been used : water is then added till every 100 volumes is diluted to 250 volumes, and another determination is made. If 90 cubic centimetres are now required to saturate the $\frac{1}{2}$ decigram alkaline solution, every 90 volumes of the acid must be diluted to 100, and the result controlled by a fresh determination ; 100 cubic centimetres of this acid should exactly saturate 5.3 grams of sodium carbonate, and will contain 1 half-decigram-molecule of acid ; 2 cubic centimetres will, therefore, contain 1 milligram-molecule (0.098 gram),† and will saturate 2 milligram-molecules of an alkali (KHO or NaHO) or 1 milligram-molecule of an alkaline carbonate (K_2CO_3 or Na_2CO_3).

To estimate the proportion of alkali in a commercial sample, a weighed portion of the substance is dissolved in water (if a solid) ; a few drops of litmus are added ; the standard acid is added from a burette, until the first permanent appearance of a light red color ; and the volume of acid employed is read off. Each cubic centimetre of acid corresponds to 1 milligram-molecule of alkali, or 1 half milligram-molecule of alkaline carbonate ; *i. e.*, to 0.053 gram of sodium carbonate, Na_2CO_3 , 0.069 gram potassium carbonate, K_2CO_3 , 0.040 gram of caustic soda, NaHO , 0.056 gram of caustic potash, KHO , and 0.017 gram of ammonia, NH_3 ; and a simple proportion gives the amount of alkali or alkaline carbonate present (*e. g.*, 100 : 6.9 :: number of cubic centimetres employed : potassium carbonate present). By operating on 100 times the $\frac{1}{2}$ milligram-molecule (*e. g.*, 6.9 grams in the case of potassium carbonate, 5.3 grams in the case of sodium carbonate) all calculation is saved : for as this amount, if present, would require 100 cubic centimetres of acid for its saturation, the number of cubic centimetres actually required at once indicates the percentage of alkaline carbonate. The burettes commonly used contain 50 cubic centimetres, and are graduated into half cubic centimetres ; so that by operating on 50 times the $\frac{1}{2}$ milligram-molecule, the number of divisions employed indicates the percentage.

Sometimes, instead of exactly neutralizing the alkali with the standard acid, it is better to add the acid till the litmus assumes a distinct light red color, then heat the solution to boiling, and add a small excess (5 to 10 cubic centimetres) of acid. The hot solution is freed from carbonic

* The molecule of sodium carbonate, Na_2CO_3 , weighs $2 \times 23 + 12 + 3 \times 16 = 106$.

† The molecular weight of sulphuric acid, H_2SO_4 , is 98 = $2 + 32 + 4 \times 16$.

ed by agitation and by drawing air through it with a glass tube; and then neutralized with a standard solution of caustic soda (100 cubic centimetres of which exactly saturate 100 cubic centimetres of the standard acid) till the color just changes from red to blue. Since the acid and alkaline solutions neutralize each other volume for volume, it is only necessary to deduct the number of cubic centimetres employed of the water from that of the former, and calculate the amount of alkali from the residue. This method, called the *indirect* or *residual method*, is preferable to the direct method previously described for the analysis of carbonates, since the change from blue to red is more distinctly marked than that from one shade of red to another.

The standard solution of caustic soda must be kept in a flask, into the neck of which is inserted a calcium chloride tube filled with a mixture of sodium sulphate and quicklime, which effectually prevents the absorption of carbonic acid. If the burette be closed with a similar tube, the soda-solution may remain in it for days.

The "alkalimeter" or "burette" is a glass tube (fig. 150) closed at one end and moulded into a spout or lip at the other, and marked with any convenient scale of equal parts, generally, as above mentioned, into 100 half cubic centimetres.* A strip of paper is pasted on the tube and suffered to dry, after which the instrument is graduated by counterpoising it in a nearly upright position in the pan of a balance of moderate delicacy, and weighing into it, in succession, 5, 10, 15, 20, etc., grams of distilled water at 4° C. until the whole quantity, amounting to 50 grams (50 cubic centimetres), has been introduced, the level of the water in the tube being, after each addition, carefully marked with a pen upon the strip of paper, while the tube is held quite upright, and the mark made between the top and bottom of the curve formed by the surface of the water. The smaller divisions of the scale, of a half cubic centimetre each, may then be made by dividing with compasses each of the spaces into ten equal parts. When the graduation is complete, and the operator is satisfied with its accuracy, the marks may be transferred to the tube itself by a sharp file, and the paper removed by a little warm water. The numbers are scratched on the glass with the hard end of the same file, or with a diamond. If the glass is covered with etching wax, the scale traced upon it with a fine needle point, and the marks etched by exposing the tube to the vapor of hydrofluoric acid.

The alkalimeter, represented in fig. 150, is the simplest form of this instrument. The pouring out of minute quantities is, however, greatly facilitated by providing the measure with a narrow dropping tube, fig. 151, the lower extremity of which is soldered into the measure, whilst the upper one is bent outward and sharply cut off. This kind of burette, which is known as Gay-Lussac's, is chiefly used in France. The liquid may be very conveniently poured from it; but it is rather easily broken, so that its manipulation requires a good deal of care. This defect is greatly obviated in the burette, fig. 152, in which the graduated tube is provided with a spout at the top, there being at the same time an orifice for pouring in the liquid.

A very elegant instrument has been contrived by Dr. Mohr, of Coblenz. It is a graduated tube, drawn out at one end to a point, to which is attached, by means of a narrow vulcanized caoutchouc tube, a short glass

Fig. 150.



* It may also be divided into 1000 grain-measures, the grain-measure being the capacity of a grain of distilled water at 60° F.; 70,000 such measures go to an imperial gallon, and 8750 to a pint.

tube, likewise drawn out to a point (fig. 153). There is a small space (about $\frac{1}{4}$ inch) between the two tubes, upon which is fixed a metallic clamp, *a*, represented in its actual dimensions in fig. 154. This clamp shuts off the connection between the graduated cylinder and the small glass tube. By pressing with the finger upon the ends *b b*, of this clamp, it opens, and allows the liquid to flow out of the lower tube. It is evident that by this

Fig. 151.



Fig. 152.

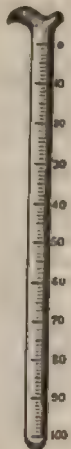


Fig. 153.

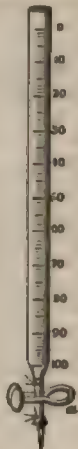
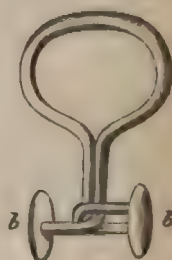


Fig. 154.

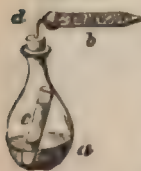


arrangement the amount of liquid may be regulated with the greatest nicety.

It is often desirable, in the analysis of carbonates, to determine directly the proportion of carbonic acid: the following methods give very exact results:—

A small light glass flask of three or four ounces capacity with lipped edge, is chosen, and a cork fitted to it. A piece of tube about three inches

Fig. 155.



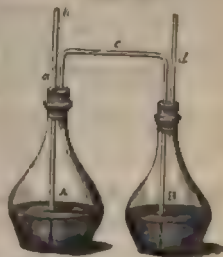
long is drawn out at one extremity, and fitted, by means of a small cork and a bit of bent tube, to the cork of the flask. This tube is filled with fragments of calcium chloride, prevented from escaping by a little cotton at either end: the joints are secured by sealing-wax. A short tube, closed at one extremity, and small enough to go into the flask, is also provided, and the apparatus is complete. Fifty grains of the carbonate to be examined are carefully weighed out and introduced into the flask, together with a little water; the small tube is then filled with oil of vitriol, and placed in the flask in a nearly upright position, and leaning against its sides

in such a manner that the acid does not escape. The cork and calcium chloride tube are then adjusted, and the whole apparatus is accurately counterpoised on the balance. This done, the flask is slightly inclined, so that the oil of vitriol may slowly mix with the other substances and decompose the carbonate, the gas from which escapes in a dry state from the extremity of the tube. When the action has entirely ceased, the liquid is heated until it boils, and the steam begins to condense in the drying-

into; it is then left to cool, and weighed, when the loss indicates the quantity of carbon dioxide. The acid must be in excess after the experiment. When calcium carbonate is thus analyzed, hydrochloric acid must be substituted for the sulphuric acid.

Instead of the above apparatus, a neat arrangement may be used, which was first suggested by Will and Fresenius. It consists of two small glass flasks, *a* and *b*, the latter being somewhat smaller than the former. Each of the flasks is provided with a doubly perforated cork. A tube, open at both ends, but closed at the upper extremity by means of a small quantity of wax, passes through the cork of *a* to the very bottom of the flask, whilst a second tube, reaching to the bottom of *b*, establishes a communication between the two flasks. The cork of *b* is provided, moreover, with a short tube, *d*. In order to analyze a carbonate, a suitable quantity (fifty grains) is put into *a*, together with some water. *a* is half filled with concentrated sulphuric acid, the apparatus tightly fitted and weighed. A small quantity of air is now sucked out of flask *a* by means of the tube *d*, whereby the air in *a* is likewise rarefied. On allowing the air to return, a quantity of the sulphuric acid ascends to the tube *c*, and flows over into flask *b*, causing a disengagement of carbon dioxide, which escapes at *d*, after having been perfectly dried by passing through the bottle *n*. This operation is repeated until the whole of the carbonate is decomposed, and the process is terminated by opening the wax stopper, and drawing a quantity of air through the apparatus. The apparatus is now reweighed. The difference of the two weighings expresses the quantity of carbon dioxide in the compound analyzed.

Fig. 156.



Sodium Sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, commonly called *Glauber's salt*, is a by-product in several chemical operations and an intermediate product in the manufacture of the carbonate as above described: it may of course be prepared directly, if wanted pure, by adding dilute sulphuric acid, to saturation, to a solution of sodium carbonate. It crystallizes in forms derived from an oblique rhombic prism: the crystals contain 10 molecules of water, are efflorescent, and undergo watery fusion when heated, like those of the carbonate: they are soluble in twice their weight of cold water, and rapidly increase in solubility as the temperature of the liquid rises to 37°C . (91.4°F .), at which point a maximum is reached, 100 parts of water dissolving 117.9 parts of the salt, corresponding with 52 parts anhydrous sodium sulphate (see fig. 95, p. 142). When the salt is heated beyond this point, the solubility diminishes, and a portion of sulphate is deposited. A warm saturated solution, evaporated at a high temperature, deposits opaque prismatic crystals, which are anhydrous. The salt has a slightly bitter taste, and is purgative. Mineral springs sometimes contain it, as that at Cheltenham.

Sodium and Hydrogen Sulphate, or *Acid Sodium Sulphate*, $2\text{NaHSO}_4 \cdot 3\text{H}_2\text{O}$ or $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, commonly called *bisulphate of soda*, is prepared by adding to 10 parts of the anhydrous neutral sulphate, 7 of oil of vitriol, evaporating the whole to dryness, and gently igniting. The acid sulphate is very soluble in water, and has an acid reaction. It is not deliquescent. When very strongly heated, the fused salt gives up anhydrous sulphuric acid (sulphuric oxide), and becomes neutral sulphate; a change which

necessarily supposes the previous formation of a pyrosulphate, $\text{Na}_2\text{S}_2\text{O}_5$, or $\text{Na}_2\text{SO}_4\cdot\text{SO}_3$.

Sodium Hyposulphite, Na_2SO_2 .—This salt is produced by the deoxidizing action of zinc on the sulphite, Na_2SO_3 . Its preparation has already been described (p. 197). It crystallizes in needles soluble in water and in weak spirit, the solution exhibiting strong bleaching and reducing properties. The crystals, when exposed to the air in the moist state, rapidly become hot from deoxidation, a property by which this salt is distinguished from the thiosulphate.

Sodium Thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, formerly called *hyposulphite*. This salt is formed from the sulphite, Na_2SO_3 , by addition of sulphur. There are several modes of procuring it. One of the best is to form neutral sodium sulphate, by passing a stream of well-washed sulphurous oxide gas into a strong solution of sodium carbonate, and then digesting the solution with sulphur at a gentle heat during several days. By careful evaporation at a moderate temperature, the salt is obtained in large regular crystals, which are very soluble in water. It is used in considerable quantities for photographic purposes, and as an antichlore.

Sodium Phosphates.—The composition and chemical relations of these salts have already been explained in speaking of the basicity of acids (p. 285).

Disodium Phosphate, or Disodic Orthophosphate; Common Tribasic Phosphate, $\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}$.—This salt is prepared by precipitating the acid calcium phosphate obtained in decomposing bone-ash with sulphuric acid, with a slight excess of sodium carbonate, and evaporating the clear liquid. It crystallizes in oblique rhombic prisms, which are efflorescent. The crystals dissolve in 4 parts of cold water, and undergo aqueous fusion when heated. The salt is bitter and purgative; its solution is alkaline to test-paper. Crystals containing 7 molecules of water, and having a form different from that above mentioned, have been obtained.

A *trisodic orthophosphate*, sometimes called *sulphosphate*, $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$, is obtained by adding a solution of caustic soda to the preceding salt. The crystals are slender six-sided prisms, soluble in five parts of cold water. It is decomposed by acids, even carbonic, but suffers no change by heat, except the loss of its water of crystallization. Its solution is strongly alkaline. *Monosodic orthophosphate*, $\text{NaH}_2\text{PO}_4\cdot \text{H}_2\text{O}$, often called *superphosphate* or *biphosphate*, may be obtained by adding phosphoric acid to the ordinary phosphate, until it ceases to precipitate barium chloride, and exposing the concentrated solution to cold. The crystals are prismatic, very soluble, and have an acid reaction. When strongly heated, this salt becomes changed into monobasic sodium phosphate, or metaphosphate.

Sodium, Ammonium, and Hydrogen Phosphate; Phosphorus Salt; Microcosmic Salt, $\text{Na}(\text{NH}_4)\text{HPO}_4\cdot 4\text{H}_2\text{O}$.—Six parts of common sodium phosphate are heated with 2 parts of water, until the whole is liquefied, and one part of powdered sal-ammoniac is added; common salt then separates, and may be removed by a filter; and from the solution, duly concentrated, the microcosmic salt is deposited in prismatic crystals, which may be purified by one or two recrystallizations. Microcosmic salt is very soluble. When gently heated, it parts with its 4 molecules of crystallization-water, and, at a higher temperature, the basic hydrogen is likewise expelled as water, together with ammonia, and a very fusible compound, sodium metaphosphate, remains, which is valuable as a flux in blow-pipe experiments. Microcosmic salt occurs in decomposed urine.

Tetrasodic Phosphate, or Sodium Pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7\cdot 10\text{H}_2\text{O}$, is prepared

by strongly heating common disodic orthophosphate, dissolving the residue in water, and recrystallizing. The crystals are very brilliant, permanent in the air, and less soluble than the original phosphate: their solution is alkali. A *sodihydric pyrophosphate* has been obtained; but it does not crystallize.

Monobasic Phosphate, or *Sodium Metaphosphate*, NaPO_3 , is obtained by heating either the acid tribasic phosphate, or microcosmic salt. It is a transparent glassy substance, fusible at a dull red heat, deliquescent, and very soluble in water. It refuses to crystallize, but dries up into a gum-like mass.

If this glassy phosphate be cooled very slowly, it separates as a beautiful crystalline mass. It may be purified by means of boiling water from the vitreous metaphosphate, which will not crystallize. Another metaphosphate has been obtained by adding sodium sulphate to an excess of phosphoric acid, evaporating, and heating to upwards of 315°C . (599°F). Possibly these several metaphosphates may be represented by the formulae NaPO_3 , $\text{Na}_2\text{P}_2\text{O}_6$, and $\text{Na}_3\text{P}_3\text{O}_9$.

The tribasic phosphates, or orthophosphates, give a bright yellow precipitate with solution of silver nitrate; the dibasic and monobasic phosphates afford white precipitates with the same substance. The salts of the two latter classes, fused with excess of sodium carbonate, are converted into orthophosphate.

Representing the phosphates intermediate in composition between the metaphosphate and pyrophosphate of sodium, discovered by Fleitmann and Henneberg, see page 290.

Sodium Borates.—The *neutral borate* or *metaborate*, NaBO_2 or $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$, is formed by fusing common borax and sodium carbonate in equivalent proportions, and dissolving the mass in water. It forms large crystals containing $\text{NaBO}_2 \cdot 3\text{H}_2\text{O}$.

The *Anhydrous borate*, *liberate*, or *Borax*, $2\text{NaBO}_2 \cdot \text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O} = \text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$, occurs in the waters of certain lakes in Thibet and Persia: it is exported in a crude state from India under the name of *tincal*. When purified, it constitutes the borax of commerce. Much borax is now, however, manufactured from the native boric acid of Tuscany, also from a native calcium borate called *hayesine*, which occurs in southern Peru. Borax crystallizes in six-sided prisms, which effloresce in dry air, and require 20 parts of cold, and 6 of boiling water for solution. On exposing to heat, the 10 molecules of water of crystallization are expelled, and at a higher temperature the salt fuses, and assumes a glassy appearance on cooling: in this state it is much used for blow-pipe experiments, the metallic oxides dissolving in it to transparent beads, many of which are distinguished by characteristic colors. By particular management, crystals of borax can be obtained with 5 molecules of water: they are very hard, and permanent in air. Borax, though by constitution an acid salt, has an alkaline reaction to test-paper. It is used in the arts for soldering metals, its action consisting in rendering the surfaces to be joined metallic, by dissolving the oxides, and it sometimes enters into the composition of the glaze with which stoneware is covered.

Sodium Sulphide, Na_2S , is prepared in the same manner as potassium monosulphide: it separates from a concentrated solution in octohedral crystals, which are rapidly decomposed by contact with the air into a mixture of sodium hydrate and thiosulphate. It forms double sulphur salts with hydrogen sulphide, carbon bisulphide, and other sulphur acids.

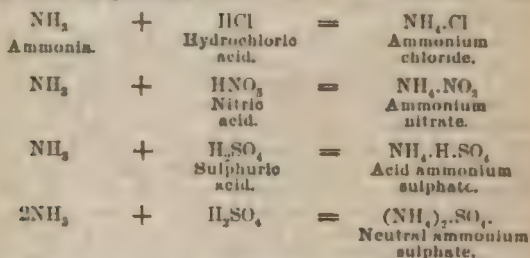
Sodium sulphide is supposed to enter into the composition of the beautiful pigment *ultramarine*, which is prepared from the *lapis lazuli*, and is

now imitated by artificial means. An intimate mixture of 37 kaolin, 15 sodium sulphate, 22 sodium carbonate, 18 sulphur, and 8 charcoal, is heated from twenty-four to thirty hours in large crucibles. The product thus obtained is again heated in cast-iron boxes at a moderate temperature till the required tint is obtained. After being finely pulverized, washed and dried, it constitutes commercial ultramarine. The composition of this color varies, and its true constitution is not known.

There is no good precipitant for sodium, all its salts being very soluble, with the exception of the *metantimonate*, which is precipitated on mixing a solution of a sodium salt with a solution of potassium metantimonate; the use of this reagent is, however, attended with some difficulties. The presence of sodium is often determined by negative evidence. The yellow color imparted by sodium salts to the outer flame of the blow-pipe, and to combustible matter, is a character of considerable importance. The spectral phenomena exhibited by sodium compounds are mentioned on page 87.

AMMONIUM.

The ammonia salts are most conveniently studied in this place, on account of their close analogy to those of potassium and sodium. These salts are formed by the direct union of ammonia, NH_3 , with acids, and as already pointed out (p. 164), they may be regarded as compounds of acid radicles, Cl , NO_3 , SO_4 , etc., with a basylous radicle, NH_4 , called ammonium, which plays in these salts the same part as potassium and sodium in their respective compounds; thus:—



The radicle NH_4 is not capable of existing in the free state, inasmuch as it contains an uneven number of monad atoms: it is simply the residue which is left on removing the atom of chlorine from the saturated molecule, NH_4Cl . Whether the double molecule

NH_4
 N_2H_6 , or $\begin{array}{c} \text{NH}_4 \\ | \\ \text{NH}_4 \end{array}$, has a separate existence, is a different question.

Ammonium is said, indeed, to be capable of forming an amalgam with mercury; but even in this state it is quickly resolved into ammonia and free hydrogen.

When a globule of mercury is placed on a piece of moistened potassium hydroxide, and connected with the negative side of a voltaic battery of very moderate power, the circuit being completed through the platinum plate upon which the alkali rests, decomposition of the latter takes place, and an amalgam of potassium is rapidly formed. If this experiment be

can be repeated with a piece of sal ammoniac instead of potassium hydroxide, a soft, solid, metalline mass is also produced, which has been called the *ammoniacal amalgam*, and considered to contain ammonium in combination with mercury. A simpler method of preparing this compound is the following: A little mercury is put into a test-tube with a grain or two of potassium or sodium, and gentle heat applied; combination ensues, attended by heat and light. When cold, the fluid amalgam is put into a capsule, and covered with a strong solution of sal-ammoniac. The production of an ammoniacal amalgam instantly commences, the mercury increasing prodigiously in volume, and becoming quite pasty. The increase of weight is, however, quite trifling: it varies from $\frac{1}{1000}$ to $\frac{1}{2000}$ part. Left to itself, the amalgam quickly decomposes into fluid mercury, ammonia, and hydrogen. It is most probable, indeed, that the so-called amalgam may be nothing more than mercury which has absorbed a certain quantity of these gases: just as silver, when heated to a very high temperature, is capable of taking up about twenty times its volume of oxygen gas, which it gives up again on cooling.*

But whether ammonium has any separate existence or not, it is quite certain that many ammoniacal salts are isomorphous with those of potassium, and if from any two of the corresponding salts, as the nitrates, KNO_3 and NH_4NO_3 , we subtract the radicle NO_3 common to the two, there remain the metal K and the group NH_4 , which are, therefore, supposed to be isomorphous.

Ammonium Chloride, Sal-ammoniac, NH_4Cl or NH_3HCl .—Sal-ammoniac was formerly obtained from Egypt, being extracted by sublimation from the soot of camel's dung: it is now largely manufactured from the ammoniacal liquid of the gas works, and from the condensed products of the distillation of bones, and other animal refuse, in the preparation of animal charcoal.

These impure and highly offensive solutions are treated with a slight excess of hydrochloric acid, by which the free alkali is neutralized, and the carbonate and sulphide are decomposed, with evolution of carbonic acid and sulphuretted hydrogen gases. The liquid is evaporated to dryness, and the salt carefully heated, to expel or decompose the tarry matter; it is then purified by sublimation in large iron vessels lined with clay, surmounted with domes of lead. Sublimed sal-ammoniac has a fibrous texture, and is tough and difficult to powder.

Sal-ammoniac separates from water under favorable circumstances, in distinct cubes or octahedrons; but the crystals are usually small, and aggregated together in rays. It has a sharp saline taste, and is soluble in $\frac{1}{2}$ parts of cold, and in a much smaller quantity of hot water. By heat, it is sublimed without decomposition. The crystals are anhydrous. Ammonium chloride forms double salts with the chlorides of magnesium, nickel, cobalt, manganese, zinc, and copper.

Ammonium Nitrate $(\text{NH}_4)\text{NO}_3$, is easily prepared by adding ammonium carbonate to slightly diluted nitric acid until neutralization has been reached. By slow evaporation at a moderate temperature it crystallizes in six-sided prisms, like those of potassium nitrate; but, as usually prepared for making nitrogen monoxide, by quick boiling until a portion solidifies completely on cooling, it forms a fibrous and indistinct crystalline mass.

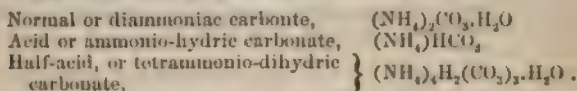
Ammonium nitrate dissolves in two parts of cold water, producing considerable depression of temperature; it is but feebly deliquescent, and

* See Watto's Dictionary of Chemistry, Supplement, p. 718.

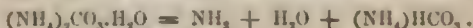
decomposes like nitre on contact with heated combustible matter. Its decomposition by heat has been already explained (p. 154).

Ammonium Sulphate $(\text{NH}_4)_2\text{SO}_4$.—Prepared by neutralizing ammonium carbonate with sulphuric acid, or on a large scale, for use as a manure, by adding sulphuric acid in excess to the coal-gas liquor just mentioned, and purifying the product by suitable means. It is soluble in 2 parts of cold water, and crystallizes in long, flattened, six-sided prisms. It is entirely decomposed and driven off by ignition, and even, to a certain extent, by long boiling with water, ammonia being expelled and the liquid rendered acid.

Ammonium Carbonates.—There are three definite carbonates of ammonium, the composition of which is as follows:—



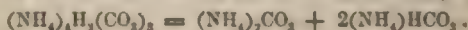
(1) The *normal carbonate* is prepared by addition of ammonia to one of the acid salts, or of water to the carbonate of ammonia, CON_2H_6 (p. 318). With certain special precautions, the description of which is too long for insertion in this work, to prevent the escape of a portion of the ammonia. It crystallizes in elongated plates or flattened prisms, having a caustic taste, a powerful ammoniacal odor, and easily giving off ammonia and water, whereby they are converted into the acid carbonate:—



(2) *Ammonium and Hydrogen Carbonate*, or *Mono-ammonic Carbonate* $(\text{NH}_4)\text{HCO}_3$, commonly called *Bicarbonate*, or *Acid carbonate of ammonia*.—This salt is obtained by saturating an aqueous solution of ammonia, or of the half-acid carbonate, with carbonic acid gas; or by treating the finely pounded half-acid carbonate with strong alcohol, which dissolves out normal or diammoniac carbonate, leaving a residue of the mono-ammonic salt. Cold water may be used instead of alcohol for this purpose; but it dissolves a larger quantity of the mono-ammonic carbonate. All ammonium carbonates when left to themselves are gradually converted into mono-ammonic carbonate. This salt forms large crystals belonging to the trimetric system. According to Deville, it is dimorphous, but never isomorphous with monopotassic carbonate; when exposed to the air, it volatilizes slowly, and gives off a faint ammoniacal odor. It dissolves in 8 parts of cold water, the solution decomposing gradually at ordinary temperatures, quickly when heated above 30°C . (86°F .), with evolution of ammonia. It is insoluble in alcohol, but when exposed to the air, under alcohol, it dissolves as normal carbonate, evolving carbon dioxide.

It has been found native in considerable quantity in the deposits of guano on the western coast of Patagonia, in white crystalline masses having a strong ammoniacal odor.

(3) *Tetrammonio-dihydric Carbonate*, $\text{N}_4\text{H}_{18}\text{C}_3\text{O}_9 = (\text{NH}_4)_4\text{H}_2(\text{CO}_3)_3$.—This salt, also called *half-acid carbonate* or *sesqui-carbonate of ammonia*, contains the elements of 1 molecule of diammoniac and 2 molecules of mono-ammonic carbonate, into which it is, in fact, resolved by treatment with water or alcohol:—



It is obtained by dissolving the commercial carbonate in strong aqueous ammonia, at about 30°C . (86°F .), and crystallizing the solution. It

forms large transparent rectangular prisms, having their summits truncated by octohedral faces. These crystals decompose very rapidly in the air, giving off water and ammonia, and being converted into mono-ammonium carbonate.

Commercial carbonate of ammonia (*sal volatile, salt of hartshorn*) consists of half-acid carbonate more or less mixed with carbamate. It is prepared on the large scale by the dry distillation of bones, hartshorn, and other animal matter, and is purified from adhering empyreumatic oil by subliming it once or twice with animal charcoal in cast-iron vessels, over which glass receivers are inverted. Another method consists in heating to redness a mixture of one part ammonium chloride or sulphate, and two parts calcium carbonate (chalk), or potassium carbonate, in a retort to which a receiver is luted.

An elaborate description of the carbonates of ammonia has been published by Dr. Divers,* to whom is due the discovery of the normal ammonium carbonate.†

Ammonium Sulphides.—Several of these compounds exist, and may be formed by distilling with sal-ammoniac the corresponding sulphides of potassium or sodium.

Ammonium and Hydrogen Sulphide, or Ammonium Hydrosulphide, (NH)₄HS, is a compound of great practical utility; it is obtained by saturating a solution of ammonia with well-washed sulphuretted hydrogen gas, until measure of the latter is absorbed. The solution is nearly colorless at first, but becomes yellow after a time, without, however, suffering material injury, unless it has been exposed to the air. It gives precipitates with most metallic solutions, which are very often characteristic, and is of great service in analytical chemistry.

Ammoniacal salts are easily recognized; they are all decomposed or volatilized at a high temperature; and when heated with calcium hydroxide or solution of alkaline carbonate, they give off ammonia, which may be recognized by its odor and alkaline reaction. The salts are all more or less soluble, the acid tartrate and the platino-chloride being, however, among the least soluble; hence, ammonium salts cannot be distinguished from potassium salts by the tests of tartaric acid and platinum solution. When a solution containing an ammoniacal salt, or free ammonia, is mixed with potash, and a solution of mercuric iodide in potassium iodide is added, a brown precipitate or coloration is immediately produced, consisting of dimercurammonium iodide, NH₂HgI:—



* Journal of the Chemical Society, 1870, pp. 171-279.

† **Ammonium Phosphate.**—The normal orthophosphate, (NH₄)₃PO₄, is formed when solution of ammonia is mixed with solution of either the other orthophosphates. It separates as a crystalline mass, dissolving when heated, and on cooling deposits crystals. It cannot be dried without loss of ammonia.

Dimersammonium orthophosphate, (NH₄)₂HPO₄.Aq. is obtained by precipitating the acid calcium orthophosphate by an excess of ammonium carbonate; calcium phosphate is separated, and the solution, by spontaneous evaporation, deposits large, colorless crystals belonging to the oblique prismatic system. It has a cooling saline taste and alkaline reaction; soluble in four parts of water and insoluble in alcohol. By exposure to air it loses water of crystallization.

Monsammonium orthophosphate, NH₄H₂PO₄.Aq. is formed by adding phosphoric acid to the previous salt, or boiling its solution until it ceases to precipitate solution of barium chloride. It crystallizes in square prisms, soluble in five parts of water, not efflorescent. Reaction slightly acid. All these orthophosphates, by exposure to a red heat, lose water and ammonia, and metaphosphoric acid, containing still some ammonia, remains. By moistening this residue with nitric acid, and again heating, all the ammonia is removed.—R. B.

This is called Nessler's test; it is by far the most delicate test for ammonia that is known.

Amic Acids and Amides.

Sulphamic Acid.—When dry ammonia gas is passed over a thin layer of sulphuric oxide, SO_3 , the gas is absorbed, and a white crystalline powder is formed, having the composition $\text{N}_2\text{H}_6\text{SO}_3$, that is, of ammonium sulphate minus one molecule of water:—

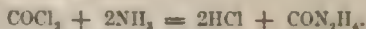


It is not, however, a salt of sulphuric acid: for its aqueous solution does not give any precipitate with baryta-water or soluble barium salts. It is, in fact, the ammonium-salt of sulphamic acid, an acid derived from sulphuric acid, SO_4H_2 or $\text{SO}_2(\text{HO})_2$, by substitution of the univalent radiæ, NH_2 (p. 318), for one atom of hydroxyl, HO . The formula is $\text{SO}_3(\text{NH}_2)\text{H}$, and that of its ammonium-salt, $\text{SO}_3(\text{NH}_2)\text{NH}_4$, or $\text{SO}_3\text{N}_2\text{H}_6$. Ammonium sulphamate is permanent in the air, and dissolves without decomposition in water. Its solution evaporated in a vacuum, over oil of vitriol, yields the salt in transparent colorless crystals.

The solution of the ammonium-salt, mixed with baryta-water, gives off ammonia, and yields a solution of *barium sulphamate* $(\text{SO}_3\text{NH}_2)_2\text{Ba}$, which may be obtained by evaporation in well-defined crystals; and the solution of this salt, decomposed with potassium sulphate, yields *potassium sulphamate*, $\text{SO}_3(\text{NH}_2)\text{K}$.

Carbamic Acid.—When dry ammonia gas is mixed with carbon dioxide, the mixture being kept cool, the gases combine in the proportion of 2 volumes of the former to 1 volume of the latter, forming a pungent, very volatile substance, which condenses in white flocks. This substance has the composition $\text{CO}_2\text{N}_2\text{H}_6$, that is, of normal ammonium carbonate $\text{CO}_3(\text{NH}_4)_2$, minus one molecule of water. It exists, as already observed, in commercial carbonate of ammonia (p. 317). It was formerly called *anhydrous carbonate of ammonia*: but, like the preceding salt, it is not really a carbonate, but the ammonium-salt of carbamic acid, $\text{CO}_2(\text{NH}_2)_2\text{H}$, an acid derived from carbonic acid, CO_3H_2 , or $\text{CO}(\text{OH})_2$, by substitution of amidogen, NH_2 , for 1 atom of hydroxyl. Ammonium carbamate dissolves readily in water, and quickly takes up one molecule of that compound, whereby it is converted into normal ammonium carbonate. When treated with sulphuric oxide, it is converted into ammonium sulphamate.

Carbamide, CON_2H_4 .—When ammonia gas is mixed with carbon oxychloride or phosgene gas, COCl_2 , a white crystalline powder is formed, having this composition:—



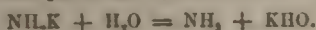
This compound, which is likewise formed in other reactions to be afterwards considered, is derived from carbonic acid $\text{CO}(\text{OH})_2$, by substitution of 2 atoms of amidogen for 2 atoms of hydroxyl. It differs from carbamic acid in being a neutral substance, not containing any hydrogen easily replaceable by metals.

Other bibasic acids likewise yield an amic acid and a neutral amide by substitution of 1 or 2 atoms of amidogen for hydroxyl. Tribasic acids yield in like manner two amic acids and one neutral amide, and tetrabasic acids may yield three amic acids and a neutral amide; thus, from pyrophosphoric acid, $\text{P}_2\text{O}_5\text{H}_4 = \text{P}_2\text{O}_3(\text{HO})_4$, are obtained the three amic acids $\text{P}_2\text{O}_5(\text{NH}_2)\text{H}_3$, $\text{P}_2\text{O}_5(\text{NH}_2)_2\text{H}_2$, and $\text{P}_2\text{O}_5(\text{NH}_2)_3\text{H}$.

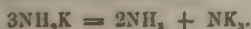
Monobasic acids, which contain but one atom of hydroxyl, yield by this mode of substitution only neutral amides, no amic acids: thus, from acetic acid, $C_2H_3O_2 = C_2H_3O.HO$, is obtained acetamide, $C_2H_3O(NH_2)$.

The neutral amides may also be regarded as derived from one or more molecules of ammonia, by substitution of univalent or multivalent acid radicals, for hydrogen: thus, acetamide $= NH_2(C_2H_3O)$; carbamide, $N_2H_4(COO)$, etc.

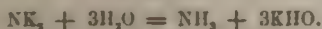
By similar substitution of metals, or basylous compound radicles, for the hydrogen of ammonia, basic compounds, called amines, are formed. Thus, when potassium is gently heated in ammonia gas, *monopotassamine*, NH_2K , is formed. It is an olive-green substance, which is decomposed by water into ammonia and potassium hydroxide:—



It melts at a little below 100, and, when heated in a close vessel, is resolved into ammonia and *tripotassamine*:—



The latter effervesces violently with water, yielding ammonia and potassium hydroxide:—



The formation and properties of amides and amines will be further considered under Organic Chemistry.

Metallammoniums.—These are hypothetical radicles derived from ammonium, N_2H_5 , by substitution of metals for hydrogen. Salts of such radicles are formed in several ways. Ammonia gas is absorbed by various metallic salts in different proportions, forming compounds, some of which may be formulated as salts of metallammoniums. Thus, platinum dichloride, $PtCl_2$, absorbs two molecules of ammonia, forming *platosammonium chloride*, $N_2H_5Pt^{IV}Cl_2$, and platinum tetrachloride, $Pt^{IV}Cl_4$, absorbs four molecules of ammonia, forming *platinammonium chloride*, $N_4H_{12}Pt^{IV}Cl_4$. In like manner, cupric chloride and sulphate form the *chloride* and *sulphate of cupsammonium*, $N_2H_5Cu^{II}Cl_2$ and $N_2H_5Cu^{II}SO_4$.

Similar compounds are formed in many cases by precipitating metallic salts with ammonia or ammoniacal salts: thus, ammonia added to a solution of mercuric chloride, $Hg^{II}Cl_2$, forms a white precipitate, consisting of *dimercurammonium chloride*, $N_2H_5Hg^{II}_2Cl_2$; and by dropping solution of mercuric chloride into a boiling solution of sal-ammoniac mixed with free ammonia, crystals are obtained, consisting of *mercurammonium chloride*, $N_2H_5Hg^{II}Cl_2$. Some of these compounds will be further considered in connection with the several metals.

LITHIUM.

Atomic weight, 7. Symbol, Li.

Lithium is found in petalite, spodumene, lepidolite, triphylline, and a few other minerals, and sometimes occurs in minute quantities in mineral springs. The most abundant source of it yet discovered is the mineral waters of Wheal Clifford in Cornwall, in which it exists to the amount of 61 parts in a million.

The metal is obtained by fusing pure lithium chloride in a small thick porcelain crucible, and decomposing the fused chloride by electricity. It is a white metal like sodium, and very oxidizable. Lithium fuses at 108° C. (356° F.); its specific gravity is 0.59: it is, therefore, the lightest solid known.

A lithium salt may be obtained from petalite on the small scale, by the following process: The mineral is reduced to an exceedingly fine powder, mixed with five or six times its weight of pure calcium carbonate, and the mixture is heated to whiteness, in a platinum crucible placed within a well-covered earthen one, for twenty minutes or half an hour. The shrunken coherent mass is digested in dilute hydrochloric acid, the whole evaporated to dryness, acidulated water added, and the silica separated by a filter. The solution is then mixed with ammonium carbonate in excess, boiled, and filtered; the clear liquid is evaporated to dryness, and gently heated in a platinum crucible, to expel the sal-ammoniac; and the residue is wetted with oil of vitriol, gently evaporated once more to dryness, and ignited: pure fused lithium sulphate then remains.

This process will serve to give a good idea of the general nature of the operation by which alkalies are extracted in mineral analysis, and their quantities determined.

Lithium hydrate, LiHO , is much less soluble in water than the hydrates of potassium and sodium; the *carbonate* and *phosphate* are also sparingly soluble salts. The *chloride* crystallizes in anhydrous cubes which are deliquescent. *Lithium sulphate* is a very beautiful salt; it crystallizes in lengthened prisms containing one molecule of water. It gives no double salt with aluminium sulphate.

The salts of lithium color the outer flame of the blow-pipe carmine-red. The spectral phenomena exhibited by lithium compounds are mentioned on page 88.

CÆSIUM AND RUBIDIUM.

Cs = 133. — Rb = 85.4.

THE two metals designated by these names were discovered by Bunsen and Kirchhoff by means of their spectrum apparatus mentioned on page 87: the former in 1860 and the latter in 1861. These metals, it appears, are widely diffused in nature, but always occur in very small quantities; they have been detected in many mineral waters, as well as in some minerals, namely, lithia-mica or lepidolite, and petalite; lately also in felspar; they have also been found in the alkaline ashes of beetroot. The salt-spring of Dürkheim, which contains 0.17 part of cesium chloride in a million parts of water, was till lately regarded as the richest source of cesium; but from recent experiments by Colonel Yorke,* it appears that the hot spring of Wheal Clifford, already mentioned as a source of lithium, contains 1.71 parts of cesium chloride in a million, or 0.12 grain in a gallon. The best material for the preparation of rubidium is lepidolite, which has been found to contain as much as 0.2 per cent. of that metal. Both metals are closely analogous to potassium in their deportment, and cannot be distinguished from that metal or from one another, either by reagents or before the blow-pipe.

Rubidium and cesium, like potassium, form double salts with tetrachloride of platinum, which are, however, much less soluble than the corre-

* *Journal of the Chemical Society*, 1872, p. 273.

expanding potassium salts: it is on this property that the separation of these metals from potassium is based. The mixture of platinochlorides is repeatedly extracted with boiling water, when a difficultly soluble residue, consisting chiefly of the platinochlorides of cesium and rubidium, remains, and these two metals are finally separated by converting them into tartrates, rubidium tartrate requiring for solution eight times as much water as cesium tartrate, and therefore crystallizing out first from the mixed solution.

The hydroxides of these metals are powerful bases, which attract carbonic acid from the air, passing, first into normal carbonate, and then into acid carbonate. Cesium carbonate is soluble in absolute alcohol; rubidium carbonate is nearly insoluble in that liquid: this property is made use of for the separation of these two metals. The chloride crystallizes in cubes, and is somewhat more soluble in water than chloride of potassium.

Rubidium chloride, when in a state of fusion, is easily decomposed by the electric current; the metal produced rises to the surface and burns with a reddish light. If this experiment be performed in an atmosphere of oxygen, to prevent oxidation, the separated metal is nevertheless lost, dissolving as it does in the fused chloride, which is transformed into a perchloride having the blue color of smalt. Rubidium, when separated under mercury by the electric current, forms a crystalline amalgam of silvery lustre, which is rapidly oxidized by the air, and decomposes water in the cold. Cesium chloride, under the influence of the electric current, exhibits exactly the same deportment as rubidium chloride. Rubidium is electro-positive towards potassium. Cesium is electro-positive towards rubidium and potassium, and thus constitutes the most electro-positive member of the elements.

GROUP II.

SILVER.

Atomic weight, 108. Symbol, Ag (Argentum).

Silver is found in the metallic state, as sulphide, in union with sulphide of antimony and sulphide of arsenic, also as chloride, iodide, and bromide. Among the principal silver mines may be mentioned those of the Harz mountains in Germany, of Kongsberg in Norway, and, more particularly, of the Andes, in both North and South America.

The greater part of the silver of commerce is extracted from ores so poor as to render any process of *smelting* or fusion inapplicable, even where fuel could be obtained, and this is often difficult to be procured. Recourse, therefore, is had to another method—that of *amalgamation*—founded on the easy solubility of silver and many other metals in metallic mercury.

The amalgamation process adopted in Germany—which differs somewhat from that in use in America—is as follows: The ore is crushed to powder, mixed with a quantity of common salt, and roasted at a low red heat in a suitable furnace, by which treatment any sulphide of silver it may contain is converted into chloride. The mixture of earthy matter, oxides of iron and copper, soluble salts, silver chloride, and metallic silver, is sifted and put into large barrels made to revolve on axes, with a quantity of water and scraps of iron, and the whole is agitated together for some time, during which the iron reduces the silver chloride to the state of metal. A

certain proportion of mercury is then introduced, and the agitation repeated: the mercury dissolves out the silver, together with gold, if there be any, also metallic copper, and other substances, forming a fluid amalgam easily separable from the thin mud of earthy matter by subsidence and washing. This amalgam is strained through a strong linen cloth, and the solid portion exposed to heat in a kind of retort, by which the remaining mercury is distilled off, and the silver left behind in an impure state.

Considerable loss often occurs in the amalgamation process from the combination of a portion of the mercury with sulphur, oxygen, etc., whereby it is brought into a pulverulent condition, known as "flouring," and is then liable to be washed away, together with the silver it has taken up. This inconvenience may be prevented, as suggested by Mr. Crookes, by amalgamating the mercury with 1 or 2 per cent. of sodium, which, by its superior affinity for sulphur and oxygen, prevents the mercury from becoming floured.

A considerable quantity of silver is obtained from argentiferous galena; in fact, almost every specimen of native lead sulphide is found to contain traces of this metal. When the proportion rises to a certain amount, it becomes worth extracting. The ore is reduced in the usual manner, the whole of the silver remaining with the lead; the latter is then re-melted in a large vessel, and allowed to cool slowly until solidification commences. The portion which first crystallizes is nearly pure lead, the alloy with silver being *more fusible than lead itself*; by particular management this is drained away, and is found to contain nearly the whole of the silver. [Pattinson's process.] This rich mass is next exposed to a red heat on the shallow hearth of a furnace, while a stream of air is allowed to impinge upon its surface; oxidation takes place with great rapidity, the fused oxide or litharge being constantly swept from the metal by the blast. When the greater part of the lead has been thus removed, the residue is transferred to a cupel or shallow dish made of bone-ashes, and again heated; the last portion of the lead is now oxidized, and the oxide sinks in a melted state into the porous vessel, while the silver, almost chemically pure, and exhibiting a brilliant surface, remains behind.

Pure silver may be easily obtained. The metal is dissolved in nitric acid; if it contains copper, the solution will have a blue tint; gold will remain undissolved as a black powder. The solution is mixed with hydrochloric acid, or with common salt, and the white, insoluble, curdy precipitate of silver chloride is washed and dried. This is then mixed with about twice its weight of anhydrous sodium carbonate, and the mixture, placed in an earthen crucible, is gradually raised to a temperature approaching whiteness, during which the sodium carbonate and the silver chloride react upon each other; carbon dioxide and oxygen escape, while metallic silver and sodium chloride result: the former melts into a button at the bottom of the crucible, and is easily detached. The following is perhaps the most simple method for the reduction of the silver chloride. The silver-salt is covered with water, to which a few drops of sulphuric acid are added; a plate of zinc is then introduced. The silver chloride soon begins to decompose, and is, after a short time, entirely converted into metallic silver; the silver thus obtained is gray and spongy; it is ultimately purified by washing with slightly acidulated water.

Pure silver has a perfect white color and a high degree of lustre: it is exceedingly malleable and ductile, and is probably the best conductor both of heat and electricity known. Its specific gravity is 10.5. In hardness, it lies between gold and copper. It melts at a bright red heat. Silver is unalterable by air and moisture: it refuses to oxidize at any temperature, but possesses the extraordinary faculty already noticed of absorbing *many times its volume of oxygen* when strongly heated in an atmosphere

of that gas, or in common air. The oxygen is again disengaged at the moment of solidification, and gives rise to the peculiar arborescent appearance often remarked on the surface of masses or buttons of pure silver. The addition of 2 per cent. of copper is sufficient to prevent the absorption of oxygen. Silver oxidizes when heated with fusible siliceous matter, as glass, which it stains yellow or orange, from the formation of a silicate. It is little attacked by hydrochloric acid; boiling oil of vitriol converts it into sulphate, with evolution of sulphurous oxide; nitric acid, even dilute, and in the cold, dissolves it readily. The tarnishing of surfaces of silver exposed to the air is due to hydrogen sulphide, the metal having a strong attraction for sulphur.

Silver Chlorides.—Two of these compounds are known, containing respectively 1 and 2 atoms of silver to 1 atom of chlorine; the second, however, is a very unstable compound.*

The *Monochloride* or *Argentio Chloride*, AgCl , is almost invariably produced when a soluble silver salt and a soluble chloride are mixed. It falls as a white, curdy precipitate, quite insoluble in water and nitric acid; one part of silver chloride is soluble in 200 parts of hydrochloric acid when concentrated, and in about 600 parts when diluted with double its weight of water. When heated it melts, and on cooling becomes a grayish crystalline mass, which cuts like horn: it is found native in this condition, constituting the *horn-silver* of the mineralogist. Silver chloride is decomposed by light, both in the dry and in the wet state, very slowly if pure, and quickly if organic matter be present: it is reduced also when put into water with metallic zinc or iron. It dissolves with great ease in ammonia and in a solution of potassium cyanide. In analysis the proportion of chlorine or hydrochloric acid in a compound is always estimated by precipitation with silver solution. The liquid is acidulated with nitric acid, and an excess of silver nitrate added; the chlorine is collected on a filter, or better, by subsidence, washed, dried, and fused; 100 parts correspond to 24.7 of chlorine, or 25.43 of hydrochloric acid.

Argentous Chloride, Ag_2Cl_2 , is obtained by treating the corresponding oxide with hydrochloric acid or by precipitating an argentous salt—the nitrate, for example—with common salt. It is easily resolved by heat or by ammonia into argentic chloride and metallic silver.

Silver Fluoride, AgF , is produced by dissolving argentic oxide or carbonate in aqueous hydrofluoric acid, and separates on evaporation in transparent quadratic octahedrons, which contain $\text{AgF} \cdot 11\frac{1}{2}\text{H}_2\text{O}$, and give off their water when fused. Their solution gives, with hydrochloric acid, a precipitate of argentic chloride. When chlorine gas is passed over fused silver fluoride, silver chloride is formed and fluorine is set free (p. 189).

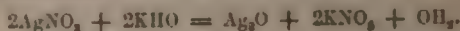
Silver Iodide, AgI , is a pale-yellow insoluble precipitate, produced by adding silver nitrate to potassium iodide; it is insoluble, or nearly so, in ammonia, and in this respect forms an exception to the silver-salts in general. Daville has obtained a crystalline silver iodide by the action of concentrated hydriodic acid upon metallic silver, which it dissolves with disengagement of hydrogen. Hydriodic acid converts silver chloride into iodide. The *bromide* of silver very closely resembles the chloride.

* The existence of two silver chlorides is utterly incompatible with the hypothesis that both silver and chlorine are monad elements. The composition of the argentous compounds is not perhaps very well established; but supposing the chloride to contain Ag_2Cl_2 , as usually stated, its constitution may be represented

by the formula $\begin{array}{c} \text{Ag}_2\text{Cl} \\ | \\ \text{Ag}_2\text{Cl} \end{array}$, in which chlorine plays the part of a triad.

Silver Oxides.—There are three oxides of silver, only one of which can, however, be regarded as a well-defined compound, namely —

The *Monoxide*, or *Argentio Oxide*, Ag_2O .—This oxide is a powerful base, yielding salts isomorphous with those of the alkali-metals. It is obtained as a pale-brown precipitate on adding caustic potash to a solution of silver nitrate:—



It is very soluble in ammonia, and is dissolved also to a small extent by pure water; the solution is alkaline. Recently precipitated silver chloride, boiled with a solution of caustic potash of specific gravity 1.25, is converted, according to Gregory, although with difficulty, into argentic oxide, which in this case is black and very dense. Argentio oxide neutralizes acids completely, and forms, for the most part, colorless salts. It is decomposed by a red heat, with evolution of oxygen, spongy metallic silver being left: the sun's rays also effect its decomposition to a small extent.

Argentous Oxide, Ag_2O^* .—When dry argentic citrate is heated to 100°C . (212°F .) in a stream of hydrogen gas, it loses oxygen and becomes dark-brown. The product, dissolved in water, gives a dark-colored solution containing free citric acid and argentous citrate, which when mixed with potash yields a precipitate of argentous oxide. This oxide is a black powder, very easily decomposed, and soluble in ammonia. The solution of argentous citrate is rendered colorless by heat, being resolved into argentic citrate and metallic silver.

Silver Dioxide, Ag_2O_2 = $\begin{array}{c} \text{AgO} \\ | \\ \text{AgO} \end{array}$.—This is a black crystalline substance

which forms upon the positive electrode of a voltaic arrangement employed to decompose a solution of silver nitrate. It is reduced by heat; evolves chlorine when acted upon by hydrochloric acid; explodes when mixed with phosphorus and struck; and decomposes solution of ammonia, with great energy and rapid disengagement of nitrogen gas.

Oxysalts of Silver.—The *nitrate*, AgNO_3 , is prepared by dissolving silver in nitric acid, and evaporating the solution to dryness, or until it is strong enough to crystallize on cooling. The crystals are colorless, transparent, anhydrous tables, soluble in an equal weight of cold and in half that quantity of boiling water: they also dissolve in alcohol. They fuse when heated, like those of nitre, and at a high temperature suffer decomposition: the *lunar caustic* of the surgeon is silver nitrate which has been melted and poured into a cylindrical mould. The salt blackens when exposed to light, more particularly if organic matters of any kind are present, and is frequently employed to communicate a dark stain to the hair: it enters into the composition of the "indelible" ink used for marking linen. The black stain has been thought to be metallic silver: it may possibly be argentous oxide. Pure silver nitrate may be prepared from the metal alloyed with copper: the alloy is dissolved in nitric acid, the solution evaporated to dryness, and the mixed nitrates cautiously heated to fusion. A small portion of the melted mass is removed from time to time for examination: it is dissolved in water, filtered, and ammonia added to it in excess. While any copper-salt remains undecomposed, the liquid will be

* Assuming that this formula is correct, and that silver is a monad, then oxysilver must be a tetrad; if, however, silver be regarded as a diad or triad, argentous oxide may be represented as $\begin{array}{c} \text{Ag} \text{---} \text{O} \text{---} \text{Ag} \\ | \\ \text{Ag} \text{---} \text{O} \text{---} \text{Ag} \end{array}$, or as $\begin{array}{c} \text{Ag} \text{---} \text{O} \text{---} \text{Ag} \\ | \\ \text{Ag} \text{---} \text{O} \text{---} \text{Ag} \end{array}$.

ble, but when that no longer happens, the nitrate may be suffered to cool, dissolved in water, and filtered from the black oxide of copper.

Silver Sulphate, Ag_2SO_4 , may be prepared by boiling together oil of vitriol and metallic silver, or by precipitating a concentrated solution of silver nitrate with an alkaline sulphate. It dissolves in 88 parts of boiling water, and separates in great measure in the crystalline form on cooling, being but slightly soluble at a low temperature. It forms with ammonia a crystallizable compound which is freely soluble in water, contains $2\text{NH}_3 \cdot \text{Ag}_2\text{SO}_4$, and may therefore be regarded as *argentammonium sulphate* $(\text{NH}_3\text{Ag})_2\text{SO}_4$.

Silver Hyposulphate, or **Dithionate**, $\text{Ag}_2\text{S}_2\text{O}_6$, is a soluble crystallizable salt, permanent in the air. The **thiosulphate**, $\text{Ag}_2\text{S}_2\text{O}_3$, is insoluble, white, and very prone to decomposition: it combines with the alkaline thiosulphates, forming soluble compounds distinguished by an intensely sweet taste. The alkaline thiosulphates dissolve both oxide and chloride of silver, and give rise to similar salts, an oxide or chloride of the alkaline metal being at the same time formed: hence the use of alkaline thiosulphates in fixing photographic pictures (p. 96).

Silver Carbonate is a white insoluble substance obtained by mixing solutions of silver nitrate and sodium carbonate. It is blackened and decomposed by boiling.

Silver Sulphide, Ag_2S , is a soft, gray, and somewhat malleable substance, found native in the crystallized state, and easily produced by melting together its constituents, or by precipitating a solution of silver with hydrogen sulphide. It is a strong sulphur-base, and combines with the sulphides of antimony and arsenic: examples of such compounds are found in the beautiful minerals, *dark and light-red silver ore*.

Ammonia Compound of Silver; Berthollet's Fulminating Silver.—This is a black, explosive compound, formed by digesting precipitated argentic oxide in ammonia. While moist, it explodes only when rubbed with a hard body, but when dry the touch of a feather is sufficient. The ammonia retains some of this substance in solution, and deposits it in small crystals by spontaneous evaporation. A similar compound exists containing oxide of gold.

Soluble silver salts are perfectly characterized by the white curdy precipitate of silver chloride, darkening by exposure to light, and insoluble in hot nitric acid, which is produced by the addition of any soluble chloride. Lead and mercury are the only metals which can be confounded with silver in this respect; but lead chloride is soluble to a great extent in boiling water, and is deposited in brilliant acicular crystals when the solution cools; and mercurous chloride is instantly blackened by ammonia, whereas silver chloride is dissolved thereby.

Solutions of silver are reduced to the metallic state by *iron, copper, mercury*, and other metals. They give with *hydrogen sulphide* a black precipitate of argentic sulphide insoluble in ammonium sulphide; with *acetic alkalies*, a brown precipitate of argentic oxide; and with *alkaline carbonates*, a white precipitate of argentic carbonate, both precipitates being easily soluble in ammonia. Ordinary *sodium phosphate* forms a yellow precipitate of argentic orthophosphate; *potassium chromate* or *bichromate*, a red-brown precipitate of argentic chromate.

The economical uses of silver are many: it is admirably adapted for culinary and other similar purposes, not being attacked in the slightest degree by any of the substances used for food. It is necessary, however,

necessarily supposes the previous formation of a pyrosulphate, $\text{Na}_2\text{S}_2\text{O}_7$, or $\text{Na}_2\text{SO}_4 \cdot \text{SO}_3$.

Sodium Hyposulphite, Na_2SO_3 .—This salt is produced by the deoxidizing action of zinc on the sulphite, Na_2SO_3 . Its preparation has already been described (p. 197). It crystallizes in needles soluble in water and in weak spirit, the solution exhibiting strong bleaching and reducing properties. The crystals, when exposed to the air in the moist state, rapidly become hot from deoxidation, a property by which this salt is distinguished from the thiosulphate.

Sodium Thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, formerly called *hyposulphite*. This salt is formed from the sulphite, Na_2SO_3 , by addition of sulphur. There are several modes of procuring it. One of the best is to form neutral sodium sulphate, by passing a stream of well-washed sulphurous oxide gas into a strong solution of sodium carbonate, and then digesting the solution with sulphur at a gentle heat during several days. By careful evaporation at a moderate temperature, the salt is obtained in large regular crystals, which are very soluble in water. It is used in considerable quantities for photographic purposes, and as an antichlore.

Sodium Phosphates.—The composition and chemical relations of these salts have already been explained in speaking of the basicity of acids (p. 285).

Disodihydric Phosphate, or Disodic Orthophosphate; Common Tribasic Phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.—This salt is prepared by precipitating the acid calcium phosphate obtained in decomposing bone-ash with sulphuric acid, with a slight excess of sodium carbonate, and evaporating the clear liquid. It crystallizes in oblique rhombic prisms, which are efflorescent. The crystals dissolve in 4 parts of cold water, and undergo aqueous fusion when heated. The salt is bitter and purgative; its solution is alkaline to test-paper. Crystals containing 7 molecules of water, and having a form different from that above mentioned, have been obtained.

A *trisodic orthophosphate*, sometimes called *subphosphate*, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, is obtained by adding a solution of caustic soda to the preceding salt. The crystals are slender six-sided prisms, soluble in five parts of cold water. It is decomposed by acids, even carbonic, but suffers no change by heat, except the loss of its water of crystallization. Its solution is strongly alkaline. *Monosodic orthophosphate*, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, often called *superphosphate* or *biphosphate*, may be obtained by adding phosphoric acid to the ordinary phosphate, until it ceases to precipitate barium chloride, and exposing the concentrated solution to cold. The crystals are prismatic, very soluble, and have an acid reaction. When strongly heated, this salt becomes changed into monobasic sodium phosphate, or metaphosphate.

Sodium, Ammonium, and Hydrogen Phosphate; Phosphorus Salt; Microcosmic Salt, $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$.—Six parts of common sodium phosphate are heated with 2 parts of water, until the whole is liquefied, and one part of powdered sal-ammoniac is added; common salt then separates, and may be removed by a filter; and from the solution, duly concentrated, the microcosmic salt is deposited in prismatic crystals, which may be purified by one or two recrystallizations. Microcosmic salt is very soluble. When gently heated, it parts with its 4 molecules of crystallization-water, and, at a higher temperature, the basic hydrogen is likewise expelled as water, together with ammonia, and a very fusible compound, sodium metaphosphate, remains, which is valuable as a flux in blow-pipe experiments. Microcosmic salt occurs in decomposed urine.

Tetrasodic Phosphate, or Sodium Pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, is prepared

The *trichloride*, or *Auric chloride*, AuCl_3 , is the most important compound of gold: it is always produced when gold is dissolved in nitro-muriatic acid. The deep yellow solution thus obtained yields, by evaporation, yellow crystals of the double chloride of gold and hydrogen; when this is cautiously heated, hydrochloric acid is expelled, and the residue, on cooling solidifies to a red crystalline mass of auric chloride, very deliquescent, and soluble in water, alcohol, and ether. Auric chloride combines with a number of metallic chlorides, forming a series of double salts, called *chloroaurates*, of which the general formula in the anhydrous state is $\text{MCl}.\text{AuCl}_3$, M representing an atom of a monad metal. These compounds are mostly yellow when in crystals, and red when deprived of water. The *ammonium salt*, $\text{NH}_4\text{Cl}.\text{AuCl}_3.2\text{H}_2\text{O}$, crystallizes in transparent needles; the *sodium salt*, $\text{NaCl}.\text{AuCl}_3.2\text{H}_2\text{O}$, in long four-sided prisms. Auric chloride likewise forms crystalline double salts with the hydrochlorides of many organic bases.

A mixture of auric chloride with excess of acid potassium or sodium carbonate is used for gilding small ornamental articles of copper: these are cleaned by dilute nitric acid, and then boiled in the mixture for some time, by which means they acquire a thin but perfect coating of reduced gold.

Oxides.—The *monoxide*, or *Aurous oxide*, is produced when caustic potash in solution is poured upon the monochloride. It is a green powder, partly soluble in the alkaline liquid; the solution rapidly decomposes into metallic gold, which subsides, and auric oxide, which remains dissolved.

Tin oxide, or *Auric oxide*, Au_2O_3 .—When magnesia is added to auric chloride, and the sparingly soluble aurate of magnesium well washed and digested with nitric acid, auric oxide is left as an insoluble reddish-yellow powder, which, when dry, becomes chestnut-brown. It is easily reduced by heat, and by mere exposure to light; it is insoluble in oxygen-acids, with the exception of strong nitric acid, insoluble in hydrofluoric acid, easily dissolved by hydrochloric and hydrobromic acids. Alkalies dissolve it freely; indeed, the acid properties of this substance are very strongly marked; it partially decomposes a solution of potassium chloride when boiled with that liquid, potassium hydroxide being produced. When digested with ammonia, it yields fulminating gold, consisting, according to Berzelius, of $\text{Au}_2\text{O}_3.4\text{NH}_3.2\text{H}_2\text{O}$.

The compounds of auric oxide with alkalies are called *aurates*. The *potassium salt*, $\text{K}_2\text{O}.\text{Au}_2\text{O}_3.6\text{H}_2\text{O}$ or $\text{KAuO}_2.3\text{H}_2\text{O}$, is a crystalline salt, the solution of which is sometimes used as a bath for electro-gilding. A compound of aurate and acid sulphite of potassium, or *potassium aurosulphite*, $2(\text{KAuO}_2.4\text{KHSO}_3).\text{H}_2\text{O}$, is deposited in yellow needles when potassium sulphite is added, drop by drop, to an alkaline solution of potassium aurate.

Gold shows but little tendency to form oxygen-salts. Auric oxide dissolves in strong nitric acid, but the solution is decomposed by evaporation or dilution. A *sodio-aurous thiosulphate*, $\text{Na}_2\text{Au}(\text{S}_2\text{O}_3)_2.2\text{H}_2\text{O}$, is prepared by mixing the concentrated solutions of auric chloride and sodium thiosulphate, and precipitating with alcohol. It is very soluble in water, and crystallizes in colorless needles. Its solution is used for fixing daguerrotype pictures. With barium chloride, it yields a gelatinous precipitate of *bario-aurous thiosulphate*, $\text{Ba}_2\text{Au}_2(\text{S}_2\text{O}_3)_4$.

Sulphides.—*Aurous sulphide*, Au_2S , is formed as a dark-brown, almost black, precipitate when hydrogen sulphide is passed into a boiling solution of auric chloride. It forms sulphur-salts with the monosulphides of potassium and sodium. *Auric sulphide*, Au_2S_3 , is precipitated in yellow flocks

when hydrogen sulphide is passed into a cold dilute solution of auric chloride. Both these sulphides dissolve in ammonium sulphide.

The presence of gold in solution may be detected by the brown precipitate with *ferrous sulphate*, fusible before the blow-pipe to a bead of metallic gold; also by the brownish-purple precipitate, called "Purple of Cassius," formed when *stannous chloride* is added to dilute gold solutions. The composition of this precipitate is not exactly known, but, after ignition, it doubtless consists of a mixture of stannic oxide and metallic gold.* It is used in enamel painting.

Oxalic acid slowly reduces gold to the metallic state; to insure complete precipitation, the gold-solution must be digested with it for 24 hours. For the quantitative analysis of a solution containing gold and other metals, oxalic acid is, in most cases, a more convenient precipitant than ferrous sulphate; inasmuch as, if the quantities of the other metals are also to be determined, the presence of a large quantity of iron-salt may complicate the analysis considerably.

Gold intended for coin, and most other purposes, is always alloyed with a certain proportion of silver or copper, to increase its hardness and durability; the first-named metal confers a pale-greenish color. English standard gold contains $\frac{1}{10}$ of alloy, now always copper. Gold, when alloyed with copper, may be estimated by fusion in a cupel with lead, in the same way as silver (p. 322). If the alloy be free from silver, the weight of the globule of gold left in the cupel will, after repeated fusions, accurately represent the quantity of gold which is present in the alloy. But, if the alloy contains silver, the metal remains with the gold after cupellation. In this case the original alloy, consisting of gold, silver, and copper, is fused in the muffle, together with lead and silver; the alloy of gold and silver remaining after cupellation is then boiled with nitric acid, which dissolves the silver, the gold being left behind. By treatment of the alloy of gold and silver with nitric acid, an accurate separation is obtained only when the two metals are present in certain proportions. If the alloy contains but little silver, that metal is protected from the action of the nitric acid by the gold; again, if it contains too much silver, the gold is left as a powder when the silver is dissolved out. Experience has shown that the most favorable proportions are $\frac{1}{2}$ gold to $\frac{1}{2}$ silver; the gold is then left pure, retaining the original shape of the alloy, and can be easily dried and weighed. The quantity of silver which is added to the alloy must therefore vary with the amount of gold which it contains.

Gold-leaf is made by rolling out plates of pure gold as thin as possible, and then beating them between folds of membrane with a heavy hammer, until the requisite degree of tenuity has been reached. The leaf is made to adhere to wood, etc., by size or varnish.

Gilding on copper has very generally been performed by dipping the articles into a solution of mercury nitrate, and then shaking them with a small lump of a soft amalgam of gold with that metal, which thus becomes spread over their surfaces: the articles are subsequently heated to expel the mercury, and then burnished. Gilding on steel is done either by applying a solution of auric chloride in ether, or by roughening the surface of the metal, heating it, and applying gold-leaf with the burnisher. Gilding by electrolysis—an elegant and simple method, now rapidly superseding many of the others—has already been noticed (p. 267). The *amalgam* usually employed is obtained by dissolving oxide or cyanide of gold in a solution of potassium cyanide.

CLASS II.—DYAD METALS.

GROUP I.—METALS OF THE ALKALINE EARTHS.

BARIUM.*

Atomic Weight, 137. Symbol, Ba.

This metal occurs abundantly as sulphate and carbonate, forming the *celestine* in many lead mines. Davy obtained it in the metallic state by means similar to those described in the case of lithium. Bunsen subjects barium chloride mixed to a paste with water and a little hydrochloric acid, at a temperature of 100°C , to the action of the electric current, using an amalgamated platinum wire as the negative pole. In this manner the metal is obtained as a solid, highly crystalline amalgam, which, when heated in a stream of hydrogen, yields barium in the form of a tumefied mass, tarnished on the surface, but often exhibiting a silver-white lustre in the cavities. Barium may also be obtained, though impure, by passing vapor of potassium over the red-hot chloride or oxide of barium. It is malleable, melts below a red heat, decomposes water, and gradually oxidizes in the air.

Barium Chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.—This valuable salt is prepared by dissolving the native carbonate in hydrochloric acid, filtering the solution, and evaporating until a pellicle begins to form at the surface: the solution on cooling deposits crystals. When native carbonate cannot be procured, the native sulphate may be employed in the following manner: The sulphate is reduced to fine powder, and intimately mixed with one-third of its weight of powdered coal; the mixture is pressed into an earthen crucible to which a cover is fitted, and exposed for an hour or more to a high red heat, by which the sulphate is converted into sulphide at the expense of the combustible matter of the coal; the black mass thus obtained is powdered and boiled in water, by which the sulphide is dissolved; and the solution, filtered hot, is mixed with a slight excess of hydrochloric acid. Barium chloride and hydrogen sulphide are then produced, the latter escaping with effervescence. Lastly, the solution is filtered to separate any little insoluble matter, and evaporated to the crystallizing point.

The crystals of barium chloride are flat four-sided tables, colorless and transparent. They contain two molecules of water, easily driven off by heat. 100 parts of water dissolve 43.5 parts at 15.5° , and 78 parts at 104.5° , which is the boiling-point of the saturated solution.

Barium Oxides.—The *Monoxide* or *Baryta*, BaO , is best prepared by decomposing the crystallized nitrate by heat in a capacious porcelain crucible until red vapors are no longer disengaged: the nitric acid is then resolved into nitrous acid and oxygen, and the baryta remains behind in the form of a grayish spongy mass, fusible at a high degree of heat. When moistened with water it combines into a hydrate, with great elevation of temperature. The *Hydroxide* or *Hydrate*, $\text{BaH}_2\text{O} = \text{BaO} \cdot \text{H}_2\text{O}$, is

* From *Barys*, heavy, in allusion to the great specific gravity of the native carbonate and sulphate.

prepared on the large scale by decomposing a hot concentrated solution of barium chloride with a solution of caustic soda; on cooling, crystals of barium hydrate are deposited, which may be purified by re-crystallization. In the laboratory barium hydrate is often prepared by boiling a strong solution of the sulphide with small successive portions of black oxide of copper until a drop of the liquid ceases to form a black precipitate with lead salts: the filtered liquid on cooling yields crystals of the hydrate. The crystals of barium hydrate contain $\text{BaH}_2\text{O}_2, 8\text{Aq.}$ * they fuse easily, and lose their water of crystallization when strongly heated, leaving the hydrate, BaH_2O_2 , in the form of a white, soft powder, having a great attraction for carbonic acid, and soluble in 20 parts of cold and 2 parts of boiling water. The solution is a valuable reagent: it is highly alkaline to test-paper, and instantly rendered turbid by the smallest trace of carbonic acid.

The *Dioxide*, BaO_2 , may be formed, as already mentioned, by exposing baryta, heated to full redness in a porcelain tube, to a current of pure oxygen gas. It is gray, and forms with water a white hydrate, which is not decomposed by that liquid in the cold, but dissolves in small quantity. Barium hydrate, when heated to redness in a current of dry atmospheric air, loses its water, and is converted, by absorption of oxygen, into barium dioxide, from which the second atom of oxygen may be expelled at a higher temperature. Boussingault has proposed to utilize these reactions for the preparation of oxygen upon a large scale. The dioxide may also be made by heating pure baryta to redness in a platinum crucible, and then gradually adding an equal weight of potassium chlorate, whereby barium dioxide and potassium chloride are produced. The latter may be extracted by cold water, and the dioxide left in the state of hydrate. It is used for the preparation of hydrogen dioxide (p. 148). When dissolved in dilute acid, it is decomposed by potassium bichromate, and by the oxide, chloride, sulphate, and carbonate of silver.

Oxysalts of Barium.—The *Nitrate*, $\text{Ba}(\text{NO}_3)_2$, is prepared by methods exactly similar to those adopted for preparing the chloride, nitric acid being substituted for hydrochloric. It crystallizes in transparent colorless octohedrons, which are anhydrous. They require for solution 8 parts of cold and 3 parts of boiling water. This salt is much less soluble in dilute nitric acid than in pure water: errors sometimes arise from such a precipitate of crystalline barium nitrate being mistaken for sulphate. It disappears on heating, or by large affusion of water.

The *Sulphate*, BaSO_4 , is found native as *heavy spar* or *barytes*, often beautifully crystallized: its specific gravity is as high as 4.4 to 4.8. This compound is always produced when sulphuric acid or a soluble sulphate is mixed with a solution of a barium salt. It is not sensibly soluble in water or in dilute acids: even in nitric acid it is almost insoluble: hot oil of vitriol dissolves a little, but the greater part separates again on cooling. Barium sulphate is now produced artificially on a large scale, and is used as a substitute for white-lead in the manufacture of oil-paints. The sulphate to be used for this purpose is precipitated from very dilute solutions: it is known in commerce as *blanc fixe*. Powdered native barium sulphate, being rather crystalline, has not sufficient body. For the production of sulphate, the chloride of barium is first prepared, which is dissolved in a large quantity of water, and then precipitated by dilute sulphuric acid.

The *Carbonate*, BaCO_3 , is found native as *witherite*, and may be formed artificially by precipitating the chloride or nitrate with an alkaline car-

* The symbol Aq. (abbreviation of *aqua*) is often used to denote water of crystallization.

oxide, or carbonate of ammonia. It is a heavy, white powder, very sparingly soluble in water, and chiefly useful in the preparation of other strontium salts.

Barium Sulphides.—The *Monosulphide*, BaS , is obtained in the manner already described (p. 329); the higher sulphides may be formed by heating it with sulphur. Barium monosulphide crystallizes from a hot solution in thin, nearly colorless plates, which contain water, and are not so soluble: they are rapidly altered by the air. A strong solution of the sulphide may be employed, as already described, in the preparation of barium hydrate.

Solutions of barium hydrate, nitrate, and chloride, are constantly kept in the laboratory as chemical tests, the first being employed to effect the separation of carbonic acid from certain gaseous mixtures, and the two latter to precipitate sulphuric acid from solution.

Soluble barium salts are poisonous, which is not the case with those of strontium. For their reactions, see page 338.

STRONTIUM.

Atomic weight, 87.6. Symbol, Sr .

The metal strontium may be obtained from its oxide by means similar to those described in the case of barium: it is usually described as a white metal, heavy, oxidizable in the air, and capable of decomposing water at common temperatures. Matthiessen states, however, that it has a dark-yellow color, and specific gravity 2.54. He prepares it by filling a small crucible having a porous cell with anhydrous strontium chloride mixed with some ammonium chloride, so that the level of the fused chloride in the cell is much higher than in the crucible. The negative pole placed in the cell consists of a very fine iron wire. The positive pole is an iron cylinder placed in the crucible round the cell. The heat is regulated so that a crust forms in the cell, and the metal collects under this crust.

Strontium Monoxide, or *Strontia*, SrO , is best prepared by decomposing the nitrate with aid of heat: it resembles baryta in almost every particular, forming, like that substance, a white hydrate, soluble in water. A hot saturated solution deposits crystals on cooling, which contain SrH_2O_2 . When heated to dull redness they lose the whole of their water, anhydrous strontia being left. The hydrate has a great attraction for carbonic acid. The *fluoride*, SrF_2 , is prepared in the same manner as barium dioxide; it may be substituted for the latter in making hydrogen dioxide.

The native carbonate and sulphate of strontium serve for the preparation of the various salts by means exactly similar to those already described in the case of barium salts: they have a very feeble degree of solubility in water.

Strontium Chloride, SrCl_2 , crystallizes in colorless needles or prisms, which are slightly deliquescent, and soluble in 2 parts of cold and a still smaller quantity of boiling water: they are also soluble in alcohol, and the solution, when kindled, burns with a crimson flame. The crystals contain 6 molecules of water, which they lose by heat: at a higher temperature the chloride fuses.

Strontium Nitrate, $\text{Sr}(\text{NO}_3)_2$, crystallizes in anhydrous octahedrons, which require for solution 5 parts of cold and about half their weight of boiling

water. It is principally of value to the pyrotechnist, who employs it in the composition of the well-known "red fire."*

The special phenomena exhibited by strontium compounds are mentioned on page 88.

CALCIUM.

Atomic weight, 40. Symbol, Ca.

CALCIUM is one of the most abundant and widely diffused of the metals, though it is never found in the free state. As carbonate, it occurs in a great variety of forms, constituting, as limestone, entire mountain ranges. Calcium was obtained in an impure state by Davy, by means similar to those adopted for the preparation of barium. Matthiessen prepares the pure metal by fusing a mixture of two molecules of calcium chloride and one of strontium chloride with some chloride of ammonium in a small porcelain crucible, in which an iron cylinder is placed as positive pole, and a pointed iron wire or a little rod of carbon connected with the zinc of the battery is made to touch the surface of the liquid. The reduced metal fuses and drops off from the point of the iron wire, and the bead is removed from the liquid by a small iron spatula. Lies-Badart and Gobin prepare calcium by igniting the iodide with an equivalent quantity of sodium in an iron crucible having its lid screwed down.

Calcium is a light yellow metal of sp. gr. 1.5778. It is about as hard as gold, very ductile, and may be cut, filed, or hammered out into plates as thin as the finest paper. It tarnishes slowly in dry, more quickly in damp air, decomposes water quickly, and is still more rapidly acted upon by dilute acids. Heated on platinum foil over a spirit-lamp, it burns with a bright flash; with a brilliant light also when heated in oxygen or chlorine gas, or in vapor of bromine, iodine, or sulphur.

Calcium Chloride, CaCl_2 , is usually prepared by dissolving marble in hydrochloric acid; it is also a by-product in several chemical manufactures. The salt separates from a strong solution in colorless, prismatic, and exceedingly deliquescent crystals, which contain 6 molecules of water. By heat this water is expelled, and by a temperature of strong ignition the salt is fused. The crystals reduced to powder are employed in the production of artificial cold by being mixed with snow or powdered ice; and the chloride, strongly dried, or in the fused state, is of great use in desiccating gases, for which purpose the latter are slowly transmitted through tubes filled with fragments of the salt. Calcium chloride is also freely soluble in alcohol, which, when anhydrous, forms with it a definite crystallizable compound.

Calcium Fluoride, Fluor-Spar, CaF_2 .—This substance is important as the most abundant natural source of hydrofluoric acid and the other fluorides. It occurs beautifully crystallized, of various colors, in lead-

| * RED FIRE: | Grains. | GREEN FIRE: | Grains. |
|-----------------------------|---------|--------------------------|---------|
| Dry strontium nitrate . . . | 800 | Dry barium nitrate . . . | 450 |
| Sulphur . . . | 225 | Sulphur . . . | 150 |
| Potassium chlorate . . . | 200 | Potassium chlorate . . . | 100 |
| Lampblack . . . | 50 | Lampblack . . . | 25 |

The strontium or barium salt, the sulphur, and the lampblack, must be finely powdered and intimately mixed, after which the potassium chlorate should be added in rather coarse powder, and mixed, without much rubbing, with the other ingredients. The red fire composition has been known to ignite spontaneously.

crystals having commonly the cubic, but sometimes the octohedral form, parallel to the faces of which latter figure they always cleave. Some varieties, when heated, emit a greenish, and some a purple phosphorescent light. The fluoride is quite insoluble in water, and is decomposed by oil of vitriol in the manner already mentioned (p. 189).

Calcium Oxides.—The *Monoxide* or *Lime*, CaO , may be obtained in a state of considerable purity by heating to full redness for some time fragments of the black bituminous marble of Derbyshire or Kilkenny. If required absolutely pure, it must be made by igniting to whiteness, in a platinum crucible, an artificial calcium carbonate, prepared by precipitating the nitrate with ammonia carbonate. Lime in an impure state is prepared for building and agricultural purposes by calcining, in a kiln of suitable construction, the ordinary limestones which abound in many districts: a red heat, continued for some hours, is sufficient to disengage the escape of the carbonic acid. In the best contrived lime-kilns the process is carried on continuously, broken limestone and fuel being constantly thrown in at the top, and the burned lime raked out at intervals from beneath. Sometimes, when the limestone contains silica, and the heat has been very high, the lime refuses to slake, and is said to be *over-burned*; in this case a portion of silicate has been formed.

Pure lime is white, and often of considerable hardness: it is quite insoluble, and phosphoresces, or emits a pale light at a high temperature. When moistened with water, it slakes with great violence, evolving heat, and crumbling to a soft, white, bulky powder, which is a hydrate containing a single molecule of water: the latter can be again expelled by a red heat. This hydrate or hydroxide, CaH_2O_2 or $\text{CaO} \cdot \text{H}_2\text{O}$, is soluble in water, but far less so than either the hydrate of barium or of strontium, and, what is very remarkable, the *colder* the water, the larger is the quantity of the compound that is taken up. A pint of water at 15.5°C . (60°F .) dissolves about 11 grains, while at 100°C . (212°F .) only 7 grains are retained in solution. The hydrate has been obtained in thin delicate crystals by slow evaporation under the air-pump. Lime-water is always prepared for chemical and pharmaceutical purposes by agitating oil-water with excess of calcium hydrate in a closely-stopped vessel, and then, after subsidence, pouring off the clear liquid, and adding a fresh quantity of water, for another operation: there is not the least occasion for filtering the solution. Lime-water has a strong alkaline reaction, a caustic taste, and when exposed to the air becomes almost instantly covered with a pellicle of carbonate, by absorption of carbonic acid. It is used, like baryta-water, as a test for carbonic acid, and also in medicine. Lime-water prepared from some varieties of limestone may contain poash.

The hardening of mortars and cements is in a great measure due to the gradual absorption of carbonic acid; but even after a very great length of time, this conversion into carbonate is not complete. Mortar is known, under favorable circumstances, to acquire extreme hardness with age. Lime-cements which resist the action of water contain iron oxides, silica, and alumina: they require to be carefully prepared, and the stone not over-heated. When they are ground to powder and mixed with water, solidification speedily ensues, from causes not yet thoroughly understood, and the cement, once in this condition, is unaffected by wet. Parker's or Roman cement is made in this manner from the nodular masses of calcareo-argillaceous ironstone found in the London clay.

Lime is of great importance in agriculture: it is found more or less in every fertile soil, and is often very advantageously added by the cultivator. The decay of vegetable fibre in the soil is thereby promoted, and other

important objects, as the destruction of certain hurtful compounds of iron in marsh and peat land, are often attained. The addition of lime probably serves likewise to liberate potassium from the insoluble silicate of that base contained in the soil.

Calcium Dioxide, CaO_2 , is said to resemble barium dioxide, and to be obtainable by treating lime with hydrogen dioxide.

Calcium Sulphate, CaSO_4 .—Crystalline native calcium sulphate, containing two molecules of water, is found in considerable abundance in some localities as *gypsum*: it is often associated with rock-salt. When regularly crystallized, it is termed *selenite*. Anhydrous calcium sulphate is also occasionally met with. The salt is formed by precipitation, when a moderately concentrated solution of calcium chloride is mixed with sulphuric acid. Calcium sulphate is soluble in about 500 parts of cold water, and its solubility is a little increased by heat. It is more soluble in water containing ammonium chloride or potassium nitrate. The solution is precipitated by alcohol. Gypsum, or native hydrated calcium sulphate, is largely employed for the purpose of making casts of statues and medals, also for moulds in the porcelain and earthenware manufactures, and for other applications. It is exposed to heat in an oven where the temperature does not exceed 127°C . (260.6°F .), by which the water of crystallization is expelled, and it is afterwards reduced to a fine powder. When mixed with water, it solidifies after a short time, from the re-formation of the same hydrate; but this effect does not happen if the gypsum has been over-heated. It is often called *Plaster of Paris*. Artificial colored marbles, or *scagliola*, are frequently prepared by inserting pieces of natural stone in a soft stucco containing this substance, and polishing the surface when the cement has become hard. Calcium sulphate is one of the most common impurities of spring water.

The peculiar property water acquires by the presence of calcium salts is termed *hardness*. It manifests itself by the effect such waters have upon the palate, and particularly by its peculiar behavior with soap. Hard water yields a lather with soap only after the whole of the calcium salts have been thrown down from the water in the form of an insoluble lime-soap. Upon this principle Clark's soap-test for the hardness of water is based. The hardness produced by calcium sulphate is called *permanent hardness*, since it cannot be remedied.

Calcium Carbonate, *Chalk; Limestone; Marble*, CaCO_3 .—Calcium carbonate, often more or less contaminated with iron oxide, clay, and organic matter, forms rocky beds, of immense extent and thickness, in almost every part of the world. These present the greatest diversities of texture and appearance, arising, in a great measure, from changes to which they have been subjected since their deposition. The most ancient and highly crystalline limestones are destitute of visible organic remains, while those of more recent origin are often entirely made up of the shelly exuviae of once living beings. Sometimes these latter are of such a nature as to show that the animals inhabited fresh water; marine species and corals are, however, most abundant. Cavities in limestone and other rocks are very often lined with magnificent crystals of calcium carbonate or calcareous spar, which have evidently been slowly deposited from a watery solution. Calcium carbonate is always precipitated when an alkaline carbonate is mixed with a solution of that base.

Although this substance is not sensibly soluble in pure water, it is freely taken up when carbonic acid happens at the same time to be present. If a little lime-water be poured into a vessel of that gas, the turbidity first produced disappears on agitation, and a transparent solution of calcium

carbonate in excess of carbonic acid is obtained. This solution is decomposed completely by boiling, the carbonic acid being expelled, and the carbonate precipitated. Since all natural waters contain dissolved carbonic acid, it is to be expected that calcium in this state should be of very common occurrence, and such is really found to be the fact, river, and more especially spring water, almost invariably containing calcium carbonate thus dissolved. In limestone districts, this is often the case to a great extent. The hardness of water, which is owing to the presence of calcium carbonate, is called *temporary*, since it is diminished to a very considerable extent by boiling, and may be nearly removed by mixing the hard water with lime-water, when both the dissolved carbonate and the dissolved lime, which thus becomes carbonated, are precipitated. Upon this principle, Dr. Clark's process of softening water is based. This process is of considerable importance, since a supply of hard water to towns in many respects a source of great inconvenience. As already mentioned, the use of such water, for the purposes of washing, is attended with a great loss of soap. Boilers, in which such water is heated, speedily become lined with a thick stony incrustation.* The beautiful stalactitic incrustations of limestone caverns, and the deposit of calc sinter or travertine upon various objects, and upon the ground, in many places, are explained by the solubility of calcium carbonate in water containing carbonic acid.

Crystallized calcium carbonate is dimorphous; calc-spar and arragonite although possessing exactly the same chemical composition, have different crystalline forms, different densities, and different optical properties. Rose has observed that calcium carbonate appears in the form of calc-spar when separated from its solution in water containing carbonic acid at the ordinary temperature. At 90°C . (194°F .), and on ebullition, however, it is slowly deposited in the form of arragonite; at lower temperatures, the formation of arragonite decreases, whilst that of calc-spar increases, the limit for the formation of the former variety being between 30° and 50°C . (86° and 122°F .).

Calc-spar occurs very abundantly in crystals derived from an obtuse rhombohedron, whose angles measure $105^{\circ} 5'$ and $74^{\circ} 55'$; its density varies from 2.5 to 2.8. The rarer variety, or arragonite, is found in crystals whose primary form is a right rhombic prism, a figure having no geometrical relation to the preceding: it is, besides, heavier and harder.

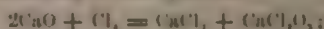
Calcium Phosphates.—A number of distinct calcium salts of phosphoric acid are known. Two tribasic phosphates or orthophosphates, $\text{Ca}_3(\text{PO}_4)_2$ and $2\text{H}(\text{PO}_4)$, are produced when the corresponding sodium salts are added in solution to calcium chloride; the first is slightly crystalline, and the second gelatinous. When the first phosphate is digested with ammonia, or dissolved in acid and re-precipitated by that alkali, it is converted into the second. The earth of bones consists principally of what appears to be a combination of these two salts. Another orthophosphate, $\text{CaH}_2(\text{PO}_4)_2$, is formed by dissolving either of the preceding in phosphoric, hydrochloric, or nitric acid, and evaporating until the salt separates, on cooling, in small platy crystals. It is the substance which yields phosphorus when heated with charcoal, in the ordinary process of manufacture before described. *Pyrophosphates* and *Metaphosphates* of calcium also exist. These

* Many proposals have been made to prevent the formation of boiler deposits. The most efficient appears to be the method of Dr. Ritterband, which consists in throwing into the boiler a small quantity of sal-ammoniac, whereby carbonate of ammoniac is formed, which is volatilized with the steam, calcium chloride remaining in solution. It need scarcely be mentioned that this plan is inapplicable in the case of permanently hard waters.

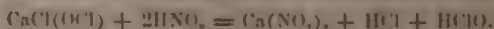
phosphates, although insoluble in water, dissolve readily in dilute acids even in acetic acid. The mineral *apatite* is chiefly calcium phosphate.

Chloride of Lime; Bleaching Powder.—When calcium hydrate, very slightly moist, is exposed to chlorine gas, the latter is readily absorbed, and a compound produced which is the bleaching powder of commerce, and is now used on an immense scale, for bleaching linen and cotton goods. It is requisite, in preparing this substance, to avoid all elevation of temperature, which may be easily done by supplying the chlorine slowly in the first instance. The product, when freshly and well prepared, is a soft, white powder, which attracts moisture from the air, and exhales an odor sensibly different from that of chlorine. It is soluble in about 10 parts of water, the unaltered hydrate being left behind: the solution is highly alkaline, and bleaches feebly. When calcium hydrate is suspended in cold water, and chlorine gas transmitted through the mixture, the lime is gradually dissolved, and the same peculiar bleaching compound produced: the alkalis, also, either caustic or carbonated, may by similar means, be made to absorb a large quantity of chlorine, and give rise to corresponding compounds; such are the "disinfecting solutions" of Labarraque.

The composition of bleaching powder is represented by the formula CaOCl_2 , and it was formerly supposed to be a direct compound of lime with chlorine. This view, however, is not consistent with its reactions, for when distilled with dilute nitric acid, it readily yields a distillate of aqueous hypochlorous acid, and when treated with water it is resolved into chloride and hypochlorite of calcium, the latter of which may be separated in crystals by exposing the filtered solution to a freezing mixture, or by evaporating it in a vacuum over oil of vitriol, and leaving the dense frozen mass to thaw upon a filter. A solution of calcium chloride mixed with hypochlorite then passes through, and feathery crystals remain on the filter, very unstable, but consisting, when recently prepared, of hydrated calcium hypochlorite, $\text{Ca}(\text{OCl})_2 \cdot 4\text{H}_2\text{O}$.^{*} These results seem at first sight to show that the bleaching powder is a mixture of chloride and hypochlorite of calcium, formed according to the equation,



but if this were its true constitution, the powder, when digested with alcohol, ought to yield a solution of calcium chloride containing half the chlorine of the original compound, which is not the case. Its constitution is therefore better represented by the formula $\text{Ca} \begin{smallmatrix} \text{Cl} \\ \text{OCl} \end{smallmatrix}$, suggested by Dr. Odling, this molecule being decomposed by water into chloride and hypochlorite in the manner just explained, and yielding, with dilute nitric or sulphuric acid, a distillate containing hydrochloric and hypochlorous acids:—

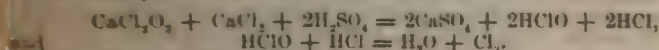


When the temperature of the calcium hydrate has risen during the absorption of the chlorine, or when the compound has been subsequently exposed to heat, its bleaching properties are impaired or altogether destroyed: it then contains chlorate and chloride of calcium, oxygen, in variable quantity, is usually set free. The same change seems to ensue by long keeping, even at the common temperature of the air. In an open vessel the compound is speedily decomposed by the carbonic acid of the air. Commercial bleaching powder thus constantly varies in value with

^{*} Kingzett, Chem. Soc. Journ. 1875, p. 404.

be age, and with the care originally bestowed upon its preparation: the best may contain about 30 per cent. of available chlorine, easily liberated by an acid, which is, however, far short of the theoretical quantity.

The general method in which this substance is employed for bleaching is the following: The goods are first immersed in a dilute solution of chlorinated lime, and then transferred to a vat containing dilute sulphuric acid. Decomposition ensues, the calcium both of the hypochlorite and of the chloride is converted into sulphate, while the free hypochlorous and hydrochloric acids yield water and free chlorine:—



The chlorine thus disengaged in contact with the cloth causes destruction of the coloring matter. The process is repeated several times, since it is unsafe to use strong solutions.

On the same principle, white patterns are imprinted upon colored cloth, the figures being stamped with tartaric acid thickened with gum-water, and then the stuff immersed in the chlorine bath, when the parts to which no acid has been applied remain unaltered, while the printed portions are bleached.

For purifying an offensive or infectious atmosphere, as an aid to proper ventilation, the bleaching powder is very convenient. The solution is exposed in shallow vessels, or cloths steeped in it are suspended in the apartment, when the carbonic acid of the air slowly decomposes it in the manner above described. Addition of a strong acid causes rapid disengagement of chlorine.

The value of any sample of bleaching powder may be easily determined by the following method, in which the feebly combined chlorine is estimated by its effect in oxidizing a ferrous salt to ferric salt, 2 molecules of ferrous oxide, FeO , requiring for this purpose 2 atoms of chlorine: the latter acts by decomposing water and liberating a corresponding quantity of oxygen. 78 (more correctly 78.16) grains of green ferrous sulphate are dissolved in about two ounces of water, and acidulated with a few drops of sulphuric or hydrochloric acid: this quantity will require for oxidation 16 grains of chlorine. Fifty grains of the chloride of lime to be examined are next rubbed up with a little tepid water, and the whole transferred to a burette (p. 310), which is then filled up to 0 with water, after which the contents are well mixed by agitation. The liquid is next gradually poured into the solution of iron, with constant stirring, until all the iron is brought to the state of ferric salt, which may be known by a drop ceasing to give a deep-blue precipitate with potassium ferrieyanide. The number of grain-measures of the chloride solution employed may then be read off: since these must contain 10 grains of serviceable chlorine, the quantity of the latter in the 50 grains may be easily reckoned. Thus, suppose 72 such measures have been taken: then

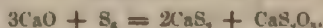
| Measures. | Grs. Chlorine. | Measures. | Grs. Chlorine. |
|-----------|----------------|-----------|----------------|
| 72 : | 10 = | 100 : | 13.89 |

The bleaching powder contains therefore 27.78 per cent.*

Calcium Sulphides.—The monosulphide, CaS , is obtained by reducing the sulphate at a high temperature with charcoal or hydrogen: it is nearly colorless, and but little soluble in water. By boiling together calcium

* Graham's Elements, vol. i. p. 593. For other methods see Watts's Dictionary of Chemistry, i. p. 904.

hydrate, water, and flowers of sulphur, a red solution is obtained, which, on cooling, deposits crystals of the bisulphide, CaS_2 , containing water. When the sulphur is in excess, and the boiling long continued, a pentasulphide is generated: thiosulphuric acid is formed as usual during these reactions:



When the yellow solution obtained by boiling lime with excess of sulphur is poured into an excess of hydrochloric acid, sulphur is precipitated together with a yellow oily liquid, which is hydrogen persulphide (p. 201): but if the acid be poured into the solution of calcium sulphide, gaseous hydrogen sulphide is given off, and the whole precipitate formed consists wholly of finely divided sulphur, the *sulphur precipitatum* of the Pharmacopœia. If dilute sulphuric acid is used, the precipitate also contains gypsum.

Calcium Phosphide.—When vapor of phosphorus is passed over fragments of lime heated to redness in a porcelain crucible, a chocolate-brown compound, the so-called *phosphuret of lime*, is produced. This substance is probably a mixture of calcium phosphide and phosphate. When thrown into water it yields spontaneously inflammable hydrogen phosphide. According to Paul Thénard, the calcium phosphide in this compound has the composition P_2Ca_2 . In contact with water it yields liquid hydrogen phosphide, P_2H_4 (p. 218).



and the greater portion of this liquid phosphide is immediately decomposed into solid and gaseous hydrogen phosphide: $5\text{P}_2\text{H}_4 = \text{P}_4\text{H}_2 + 6\text{PH}_3$.

Reactions of the Alkaline Earth-metals in solution.—Barium, strontium, and calcium are thus distinguished from all other substances, and from each other.

Caustic Potash, when free from carbonate, and caustic ammonia, occasion no precipitates in dilute solutions of the alkaline earths, especially of the first two, the hydrates being soluble in water.

Alkaline carbonates, and *carbonate of ammonium*, give white precipitates, insoluble in excess of the precipitant, with all three.

Sulphuric acid, or a *sulphate*, added to very dilute solutions of the salts of these metals, gives an immediate white precipitate with barium salts; a similar precipitate after a short interval with strontium salts; and occasions no change with calcium salts. The precipitates with barium and strontium salts are insoluble in nitric acid.

Solution of *calcium sulphate* gives an instantaneous cloud with barium salts, and one with strontium salts after a little time.

Strontium sulphate is itself sufficiently soluble to occasion turbidity when mixed with barium chloride.

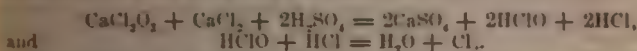
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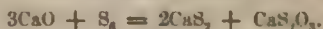
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APPENDIX TO GROUP I.

METALS OF THE EARTHS.

The metals belonging to this group are beryllium, yttrium, erbium, lanthanum, didymium, cerium, aluminium, zirconium, and thorium. Beryllium is a dyad; yttrium, erbium, lanthanum, didymium, and cerium (in the cerous compounds), have hitherto been regarded as dyads; but recent observations have shown that they are more probably triads. Aluminium is also a triad; zirconium and thorium are tetrads. All these metals form oxides of earthy character.

ALUMINIUM.

Atomic weight, 27.4. Symbol, Al.

This metal occurs very abundantly in nature in the state of silicate, as in felspar and its associated minerals; also in the various modifications of clay thence derived. It was first isolated by Wöhler, who obtained it as a gray powder by decomposing aluminium chloride with potassium; and H. Sainte-Claire Deville, by an improved process founded on the same principle, has succeeded in obtaining it in the compact form and on the manufacturing scale. The process consists in decomposing the double chloride of aluminium and sodium, $\text{AlCl}_3 \cdot \text{NaCl}$, by heating it with metallic sodium, fluor-spar or cryolite being added as a flux. The reduction is effected in crucibles, or on the large scale on the hearth of a reverberatory furnace. Sodium is used as the reducing agent in preference to potassium: first, because it is more easily prepared; and, secondly, because it has a lower atomic weight, and, consequently, a smaller quantity of it suffices to do the same amount of chemical work.

Aluminium is also prepared directly from cryolite by reduction with sodium, but the metal thus obtained is said to be more contaminated with iron and silicon than that prepared by Deville's process.

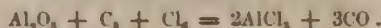
Aluminium is remarkable for its low specific gravity, which is 2.6: it is nearly as white as silver, and is capable of assuming a high polish. It is employed in the manufacture of delicate apparatus and ornamental articles. Some of the alloys of aluminium promise to become more generally applicable, more especially the alloy with copper, which is remarkable for being similar in appearance to gold; this alloy is found in commerce under the name of aluminium bronze.

Aluminium forms only one class of compounds, in which it is trivalent, one atom of the metal being equivalent to three atoms of hydrogen; thus the chloride is AlCl_3 , the oxide, Al_2O_3 , etc.

Aluminium Chloride, AlCl_3 .—This compound is obtained in solution by dissolving alumina or aluminium hydrate in hydrochloric acid; but the solution, when evaporated, gives off hydrochloric acid and leaves alumina. The anhydrous chloride may be prepared by heating a mixture of alumina and finely divided carbon in chlorine gas.

Pure precipitated alumina is dried and mixed with oil and lampblack, and the mixture, after being strongly calcined in a covered crucible, is

introduced into a porcelain tube or tubulated earthen retort placed in a furnace, and connected at one end with an apparatus for evolving chlorine, and at the other with a dry receiver. On raising the heat to bright redness, and passing chlorine through the apparatus, aluminium chloride distils over, together with carbon monoxide, and condenses as a solid mass in the receiver:—



Aluminium chloride is a transparent, waxy substance, having a crystalline structure, colorless when pure, but generally exhibiting a yellow color, due, perhaps, to the presence of iron. It boils at about 180° , fumes in the air, and smells of hydrochloric acid. It is very deliquescent, and dissolves readily in water; the solution when left to evaporate yields the hydrated chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, in six-sided prisms, which when heated are resolved into alumina and hydrochloric acid.

Aluminium and Sodium Chloride, $\text{AlCl}_3 \cdot \text{NaCl}$, is obtained by melting together the component chlorides in proper proportions, or by adding the requisite quantity of sodium chloride to the mixture of alumina and charcoal used for the preparation of aluminium chloride, igniting the mass in chlorine or hydrochloric acid, and condensing the vapor in a receiver. It is a crystalline mass, less deliquescent than aluminium chloride, and, therefore, more convenient for the preparation of aluminium.

Aluminium Fluoride, AlF_3 , is produced by the action of gaseous silicon fluoride on aluminium, and forms cubic crystals, volatilizing at a red heat, insoluble in water, and resisting the action of all acids.

Aluminium and Sodium Fluoride, $\text{AlF}_3 \cdot 3\text{NaF}$, occurs abundantly as cryolite, at Evigtok in Greenland, and is prepared artificially by pouring hydrofluoric acid in excess on a mixture of calcined alumina and sodium carbonate. Cryolite forms quadratic crystals, colorless, transparent, softer than felspar, and of specific gravity 2.96. It is used, as already mentioned, for the preparation of aluminium, and in Germany for the manufacture of soda for the use of soap-boilers.

Aluminium Oxide.—**Alumina**, Al_2O_3 .—This substance is inferred to be a sesquioxide from its isomorphism with ferric oxide. It is prepared by mixing a solution of alum with excess of ammonia, by which an extremely bulky, white, gelatinous precipitate of aluminium hydrate is thrown down. This is washed, dried, and ignited to whiteness. Thus obtained, alumina constitutes a white, tasteless, coherent mass, very little acted upon by acids. It is fusible before the oxy-hydrogen blowpipe. The mineral called *corundum*, of which the ruby and sapphire are transparent varieties, consists of nearly pure alumina in a crystallized state, with a little coloring oxide: emery, used for polishing glass and metals, is a coarse variety of corundum. Alumina is a very feeble base, and its salts have often an acid reaction.

Aluminium Hydrates.—Aluminium forms three hydrates; namely:—

| | |
|-----------------------|--|
| Monohydrate | AlHO_2 or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |
| Dihydrate | $\text{Al}_2\text{H}_2\text{O}_5$ or $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ |
| Trihydrate | AlH_3O_6 or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ |

The monohydrate is found native, as *diaspore*, in translucent masses, which crumble to powder when heated, and give off the whole of their water at 360°C . (680°F .).

The trihydrate is the ordinary gelatinous precipitate obtained by treating solutions of aluminium-salts—alum, for example, with ammonia or alkali.

line carbonates. When dried at a moderate heat, it forms a soft friable mass, which adheres to the tongue and forms a stiff paste with water, but does not dissolve in that liquid. At a strong red heat, it gives off water, and undergoes a very great contraction of volume. It dissolves with great facility in acids, and in the fixed caustic alkalies. When a solution of alumina in caustic potash is exposed to the air, the potash absorbs carbonic acid, and the aluminium trihydrate is then deposited in white crystals, which are but sparingly soluble in acids.

Aluminium trihydrate has a very powerful attraction for organic matter, and when digested in solutions of vegetable coloring matter, combines with and carries down the coloring matter, which is thus removed entirely from the liquid if the alumina is in sufficient quantity. The pigments called *lutes* are compounds of this nature. The fibre of cotton impregnated with alumina acquires the same power of retaining coloring matters; hence the great use of aluminous salts as *mordants* to produce fast colors.

Aluminium trihydrate occurs native as *Gibbsite*, a stalactitic, translucent, fibrous mineral, easily dissolved by acids.

Dihydrate.—When a dilute solution of aluminium diacetate is exposed for several days to a temperature of 100° in a close vessel, the acetic acid appears to be set free, although no precipitation of alumina takes place. The liquid acquires the taste of acetic acid, and if afterwards boiled in an open vessel, gives off nearly the whole of its acetic acid, the alumina, nevertheless, remaining in solution. This solution is coagulated by mineral acids and by most vegetable acids, by alkalies, and by decoctions of dye-woods. The alumina contained in it is, however, no longer capable of acting as a mordant. Its coagulum with dye-woods has the color of the infusion, but is translucent and totally different from the dense opaque laves which ordinary alumina forms with the same coloring matters. On evaporating the solution to dryness at 100° C. (212° F.), the alumina remains in the form of dihydrate, retaining only a trace of acetic acid. In this state it is insoluble in the stronger acids, but soluble in acetic acid, provided it has not been previously coagulated in the manner just mentioned. Boiling potash converts it into the trihydrate.*

Aluminates.—The hydrogen in aluminium trihydrate may be replaced by an equivalent quantity of various metals; such compounds are called *aluminates*. According to Frémy, a solution of alumina in potash slowly evaporated, out of contact with the air, deposits granular crystals of potassium aluminate, AlKO_2 , or $\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O}$. Similar compounds occur nature; thus, *Spinel* is an aluminate of magnesium, Al_2MgO_4 ; *Gahnite*, an aluminate of zinc, Al_2ZnO_4 .

Aluminium Sulphide, Al_2S_3 .—When the vapor of carbon bisulphide is passed over alumina, at a bright red heat, a glassy melted mass remains, which is instantly decomposed by water, with evolution of sulphuretted hydrogen.

Aluminium Sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, or $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 18\text{H}_2\text{O}$.—Prepared by saturating dilute sulphuric acid with aluminium hydrate, and evaporating; or, on the large scale, by heating clay with sulphuric acid. It crystallizes in thin pearly plates, soluble in 2 parts of water: it has a sweet and astringent taste, and an acid reaction. Heated to redness, it is decomposed, leaving pure alumina. Two other aluminium sulphates, with excess of base, are also described, one of which is insoluble in water.

Aluminium sulphate combines with sulphates of potassium, sodium, and ammonium, and the other alkali-metals, forming double salts of great interest, the *alums*. Common alum, the source of all the preparations of alumina, contains $\text{AlK}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$. It is manufactured on a very large scale from a kind of slaty clay loaded with iron bisulphide, which abounds in certain localities. This is gently roasted, and then exposed to the air in a moistened state; oxygen is absorbed; the sulphur becomes acidified; ferrous sulphate and aluminium sulphate are produced, and afterwards separated by lixiviation with water. The solution is next concentrated, and mixed with a quantity of potassium chloride, which decomposes the iron-salt, forming ferrous chloride and potassium sulphate: the latter combines with the aluminium sulphate to form alum. By crystallization, the alum is separated from the highly soluble iron chloride, and afterwards easily purified by a repetition of the process. Other methods of alum-making are sometimes employed.

Potassium-alum crystallizes in colorless, transparent octohedrons which often exhibit the faces of the cube. It has a sweetish and astringent taste, reddens litmus-paper, and dissolves in 18 parts of water at 15.5° , and its own weight of boiling water. Exposed to heat, it is easily rendered anhydrous, and by a very high temperature it is decomposed. The crystals have little tendency to change in the air. Alum is largely used in the arts, in preparing skins, dyeing, etc.: it is occasionally contaminated with iron oxide, which interferes with some of its applications. The celebrated Roman alum, made from *alum-stone*, a felspathic rock altered by sulphurous vapors, was once much prized on account of its freedom from this impurity. A mixture of dried alum and sugar, carbonized in an open pan, and then heated to redness in a glass flask, contact with air being avoided, furnishes the *Homburg's pyrophorus*, which ignites spontaneously on exposure to the air. The essential ingredient is, in all probability, finely-divided potassium sulphide.

A process has lately been patented by Messrs. Duncan and Newlands for separating the potash from syrups of beet and cane-sugar by means of aluminium sulphate, the potash being thereby precipitated in the form of alum. A solution of aluminium sulphate of a density corresponding with about 27° of Baume's hydrometer, is added to the cold syrup having a density of about 36° B. in quantity sufficient to precipitate the whole of the potash present; the mixture is well stirred for fifteen minutes to an hour; and the whole left at rest for four or five hours till the deposit has completely subsided. This deposit consists of small crystals, technically known as "*alum-meal*." Considerable quantities of alum are now made by this process.

Sodium-alum, in which sulphate of sodium replaces sulphate of potassium, has a form and constitution similar to that of common alum: it is, however, much more soluble, and difficult to crystallize.

Ammonium-alum, containing NH_4 , instead of K, very closely resembles common potassium-alum, having the same figure, appearance, and constitution, and nearly the same degree of solubility as that substance. It is manufactured for commercial use. As the value of potassium-salts is continually increasing, ammonium-alum, which may be used in dyeing with the same advantage as the corresponding potassium-salt, has almost entirely replaced the potassium-alum. When heated to redness, ammonium-alum yields pure alumina.

Cesium-alum, $\text{AlCs}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, and *Rubidium-alum*, $\text{AlRb}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, resemble potassium-alum. A *silver-alum*, $\text{AlAg}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, is formed by heating equivalent quantities of argentic and aluminium sulphates till the former is dissolved. It crystallizes in regular octohedrons, and is

redissolved by water into its component salts. There is also a *thallium-alum*, $\text{AlTh}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, which crystallizes in regular octohedrons.

Lastly, there are alums isomorphous with those just described, in which the trivalent aluminium is replaced by trivalent iron, chromium, and manganese: for example, potassio-ferric sulphate or potassium-iron alum, $\text{FeK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; ammonio-chromic sulphate, $\text{Cr}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. These will be described further on.

Few other aluminium salts present especial interest, except the silicates; but these latter are of great importance. Silicates of aluminium enter into the composition of a number of crystallized minerals, among which feldspar, by reason of its abundant occurrence, occupies a prominent place. Granite porphyry, trachyte, and other ancient unstratified rocks, consist in great part of this mineral, which, under peculiar circumstances, by no means well understood, and particularly by the action of the carbonic acid of the air, suffers complete decomposition, being converted into a soft, friable mass of earthy matter. This is the origin of clay: the change itself is seen in great perfection in certain districts of Devonshire and Cornwall, the feldspar of the fine white granite of those localities being often disintegrated to a great depth, and the rock altered to a substance resembling soft mortar. By washing, this finely divided matter is separated from the quartz and mica; and the milk-like liquid, being stored up in tanks, deposits the suspended clay, which is afterwards dried, first in the air, and afterwards in a stove, and employed in the manufacture of porcelain. The composition assigned to unaltered feldspar is AlKSi_3O_8 , or $\text{AlKSiO}_3 \cdot 2\text{SiO}_2$, or $\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 6\text{SiO}_2$. The exact nature of the change by which feldspar passes into porcelain clay is unknown, although it evidently consists in the abstraction of silica and alkali.

When the decomposing rock contains iron oxide, the clay produced is colored. The different varieties of shale and slate result from the alteration of ancient clay-beds, apparently in many instances by the infiltration of water holding silica in solution: the dark appearance of some of these deposits is due to bituminous matter.

It is a common mistake to confound clay with alumina: all clays are essentially silicates of that base; they often vary a good deal in composition. Dilute acids exert little action on these compounds; but by boiling with oil of vitriol, alumina is dissolved out, and finely divided silica left behind. Clays containing an admixture of calcium carbonate are termed *marls*, and are recognized by effervescing with acids.

A basic aluminium silicate, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, is found crystallized, constituting the beautiful mineral called *cyanite*. The compounds formed by the union of the aluminium silicates with other silicates are almost innumerable. A sodium feldspar, *albite*, containing that metal in place of potassium, is known, and there are two somewhat similar lithium compounds, *spodumene* and *psilade*. The *zeolites* are hydrated silicates belonging to this class; *nauphase*, *apheline*, *mesotype*, etc., are double silicates of sodium and aluminium, with water of crystallization. *Stilbite*, *heulandite*, *laumontite*, *prehnite*, etc., consist of calcium silicate combined with silicate of aluminium. The *glaucos*, *arinite*, *mica*, etc., have a similar composition, but are anhydrous. Iron sesquioxide is very often substituted for alumina in these minerals.

Salts of aluminium, when moistened with *cobalt nitrate* and heated before the blow-pipe, assume a characteristic blue color.

Alumina, when in solution, is distinguished without difficulty. Caustic potash and soda occasion a white gelatinous precipitate of aluminium hydrate, freely soluble in excess of the alkali. Ammonia produces a similar precipitate, insoluble in excess of the reagent. The alkaline carbonates

and carbonate of ammonium precipitate the hydrate, with escape of carbonic acid. The precipitates are insoluble in excess.

Ammonium sulphide also produces a white precipitate of aluminium hydrate.

BERYLLIUM, or GLUCINUM.

Atomic weight, 9.4. Symbol, Be.

This somewhat rare metal occurs as a silicate, either alone as in phenacite, or associated with other silicates, in beryl, emerald, euclase, leucophane, helvite, and several varieties of gadolinite; also as an aluminate in chrysoberyl or cymophane.

Metallic beryllium is obtained by passing the vapor of the chloride over melted sodium. It is a white metal of specific gravity 2.1; it may be forged and rolled into sheets like gold; its melting point is below that of silver. It does not decompose water at the boiling heat. Sulphuric and hydrochloric acids dissolve it, with evolution of hydrogen.

Beryllium forms but one class of compounds, and there is considerable doubt as to its atomic weight and equivalent value. On the one hand, it is regarded as a dyad, like calcium and magnesium, with the atomic weight 9.4, its chloride being BeCl_2 , its oxide, BeO ; on the other hand, as a triad, like aluminium, on which supposition its chloride would be BeCl_3 , its oxide Be_2O_3 , and its atomic weight 14; but the former view appears, on the whole, to be most in accordance with observed facts.

Beryllium Chloride, BeCl_2 . is formed by heating the metal in chlorine or hydrochloric acid gas, or by the action of aqueous hydrochloric acid on the metal or its oxide.

The anhydrous chloride is prepared by passing chlorine over an ignited mixture of beryllia and charcoal. It is less volatile than aluminium chloride, very deliquescent, and easily soluble in water.

Beryllium Oxide.—Beryllia, BeO .—This earth may be prepared from beryl, or either of the other beryllium silicates, by fusing the finely pounded mineral with potassium carbonate or quicklime; treating the fused mass with hydrochloric acid; evaporating to dryness; then moistening the residue with hydrochloric acid, and treating it with water, whereby everything is dissolved except the silica. The filtered liquid is then mixed with excess of ammonia solution, which throws down a bulky precipitate containing both alumina and beryllia; this precipitate is well washed, and the beryllia is dissolved out from the alumina by digestion in a cold strong solution of ammonium carbonate. The liquid is again filtered, and on boiling it, beryllium carbonate is deposited as a white powder, which, when ignited, leaves pure beryllia.

Beryllia is very much like alumina in physical characters, and further resembles that substance in being readily dissolved by caustic potash or soda; but it is distinguished from alumina by its solubility, when recently precipitated, in a cold solution of ammonium carbonate. Beryllium salts have a sweet taste, whence the former name of the metal, *glucinum* (from *γλυκύς*). They are colorless, and are distinguished from those of aluminium by not yielding an alum with potassium sulphate, nor a blue color when heated before the blowpipe with cobalt nitrate, also by their reaction with ammonium carbonate.

ZIRCONIUM.

Atomic weight, 89.6. Symbol, Zr.

This is a tetrad metal, intermediate in many of its properties between aluminium and silicon. Its oxide, zirconia, was first obtained by Klaproth, in 1789, from zircon, which is a silicate of zirconium. It has since been found in fergusonite, endialyte, and two or three other rare minerals.

Zirconium, like silicon, is capable of existing in three different states, amorphous, crystalline, and graphitoid. The amorphous and crystalline varieties are obtained by processes similar to those described for preparing the corresponding modifications of silicon; graphitoid zirconium was obtained, by Troost, in attempting to decompose sodium zirconate with iron in light scales of a steel-gray color. Amorphous zirconium when heated in the air takes fire at a heat somewhat below redness, and burns with a bright light, forming zirconia. Crystalline zirconium forms very hard brittle scales resembling antimony in color and lustre; it burns in the air only at the heat of the oxy-hydrogen blowpipe, but takes fire at a red heat in chlorine gas. Zirconium is but little attacked by the ordinary acids; but hydrofluoric acid dissolves it readily, with evolution of hydrogen.

Zirconium Oxide, or Zirconia, ZrO_2 , is prepared by strongly igniting zircon (zirconium silicate), with four times its weight of dry sodium carbonate and a small quantity of sodium hydrate. The silica is separated from the fused mass by hydrochloric acid, as described in the case of beryl. The resulting solution is treated with ammonia, which throws down zirconia generally mixed with ferric oxide; the precipitate is redissolved in hydrochloric acid; and the solution is boiled with excess of sodium thiosulphate as long as sulphurous acid continues to escape, thereby pure zirconia is precipitated, the whole of the iron remaining in the solution. Zirconia thus obtained forms a white powder, or hard lumps, of specific gravity 4.35 to 4.9. By fusing it with borax in a pottery furnace and dissolving out the soluble salts with hydrochloric acid, zirconia is obtained in small quadratic prisms isomorphous with the native oxides of tin and titanium.

Zirconium hydrates are obtained by precipitating the solution of a zirconium salt with ammonia; the precipitate contains $ZrH_2O_3 = ZrO_2 \cdot H_2O$, or $ZrH_4O_4 = Zr_2 \cdot 2H_2O$, according to the temperature at which it is dried.

Zirconia acts both as a base and as an acid. After ignition it is insoluble in all acids except hydrofluoric and very strong sulphuric acid, but the hydrate dissolves easily in acids, forming the zirconium salts; the normal sulphate has the composition $Zr(SO_4)_2$, or $ZrO_2 \cdot 2SO_3$.

Compounds of zirconia with the stronger bases, called zirconates, are obtained by precipitating a zirconium salt with potash or soda, or by igniting zirconia with an alkaline hydrate. Potassium zirconate dissolves completely in water. Three sodium zirconates have been formed, containing $Na_2ZrO_3 = Na_2O \cdot ZrO_2$; $Na_4ZrO_4 = 2Na_2O \cdot ZrO_2$; and $Na_6Zr_2O_7 = Na_2O \cdot 3ZrO_2$.

Zirconium Fluoride, ZrF_4 .—This compound is obtained by dissolving zirconia, or the hydrate, in hydrofluoric acid; or in the anhydrous state, by igniting zirconia with ammonium and hydrogen fluoride till all the ammonium fluoride is driven off. It unites with other metallic fluorides,

forming double salts, called zirconfluorides or fluozirconates, which are isomorphous with the corresponding silicofluorides, stannofluorides, and titanofluorides, and are mostly represented by the formula—



in which M denotes a monad metal. The sodium salt, however, has the composition $5NaF.3ZrF_6$.

THORINUM or THORIUM.

Atomic weight, 231.5. Symbol, Th.

This very rare metal was discovered in 1828 by Berzelius, in thorite, a mineral from the Norwegian island Lovön, in which it exists as a silicate. It has since been found in euxenite, pyrochlore, and a few other minerals, all very scarce.

Metallic thorium is obtained by reducing the chloride with potassium or sodium, as a gray powder, which acquires metallic lustre by pressure, and has a density of 7.66 to 7.9. It is not oxidized by water, dissolves easily in nitric, slowly in hydrochloric acid, and is not attacked by caustic alkalis.

Thorium forms but one class of compounds, in all of which it is quadrivalent.

Thorium Oxide, or Thorina, ThO_2 , is prepared by decomposing thorite with hydrochloric acid, separating the silica in the usual way, treating the filtered solution with hydrogen sulphide to separate lead and tin, and precipitating the thorina by ammonia, together with small quantities of the oxides of iron, manganese, and uranium. To get rid of these, the precipitate is redissolved in hydrochloric acid, and the hot saturated solution is boiled with a solution of neutral potassium sulphate. The thorium is thereby precipitated as thorium and potassium sulphate; and from the solution of this salt in hot water, the thorium is precipitated by alkalis as a hydrate, which, on ignition, yields pure thorina.

Thorina is white, and very heavy, its specific gravity being 9.402. After ignition, it is insoluble in nitric and hydrochloric acids, and dissolves in strong sulphuric acid only after prolonged heating. The *hydrate*, precipitated from thorium salts by alkalis, dissolves easily in acids.

Thorium Chloride, $ThCl_4$, prepared by igniting an intimate mixture of thorina and charcoal in chlorine gas, sublimes in white shining crystals. It forms double salts with the chlorides of the alkali-metals.

Thorium Sulphate, $Th(SO_4)_2$, crystallizes with various quantities of water, according to the temperature at which its solution is evaporated. *Thorium and potassium sulphate, $ThK_4(SO_4)_6.2H_2O$,* separates as a crystalline powder when a crust of potassium sulphate is suspended in a solution of thorium sulphate. It is easily soluble in water, but insoluble in alcohol and in solution of potassium sulphate.

CERIUM.—LANTHANUM.—DIDYMIUM.

Ce = 138. — La = 139. — Di = 114.75.

THESE three metals occur together as silicates in the Swedish mineral cerite, also in allanite, orthite, and a few others; and as phosphates in monazite, edwardsite, and cryptolite, a mineral occurring disseminated through apatite and through certain cobalt ores.

Cerium was discovered in 1803 by Klaproth, and by Hisinger and Berzelius, who obtained it in the form of oxide from cerite. This mineral is completely decomposed by boiling with strong hydrochloric acid, silica being separated, and the cerium, together with iron and other metals, dissolving as chloride. On treating the acid solution thus obtained with oxalic acid, cerium oxalate is precipitated as a white crystalline powder, which, when ignited, leaves a brown oxide. The product thus obtained was, for some time, regarded as the oxide of a single metal, cerium; but, in 1839 and 1841, Mosander* showed that it contained the oxides of two other metals, which he designated as lanthanum† and didymium‡.

Cerium oxide may be separated from the oxides of lanthanum and didymium by treating the crude brown oxide above mentioned, first with dilute and then with strong nitric acid, which gradually removes the whole of the lanthanum and didymium oxides.

The separation of these two oxides one from the other is much more difficult, and can be effected only by successive crystallization of their sulphates. If the lanthanum salt is in excess, in which case the solution of the mixed sulphates has only a faint amethyst tinge, the liquid is evaporated to dryness, and the residue heated to a temperature just below red-heat, to render the sulphates anhydrous. The residue thus obtained is then to be added by small portions to ice-cold water, which dissolves it easily, and the resulting solution heated in a water-bath to about 40°. Lanthanum sulphate then crystallizes out, containing only a small quantity of didymium, and may be further purified by repeating the whole process. If, on the other hand, the didymium-salt is in excess, in which case the liquid has a decided rose-color, separation may be effected by leaving the acid solution in a warm place for a day or two. Didymium sulphate then separates in large rhombohedral crystals.

Metallie cerium, lanthanum, and didymium are obtained by reducing the chlorides with sodium, in the form of gray powders, which decompose water at ordinary temperatures, and dissolve rapidly in dilute acids with evolution of hydrogen.

Atomic Weights and Quantivalence.—According to the atomic weights hitherto assigned to these three metals, viz.: Ce = 92, La = 93.6, Di = 95 (see Table on page 27), lanthanum and didymium should be dyads, forming chlorides and oxides of the types RCl_2 and RO , and cerium should be classed with the iron-metals. Mendelejeff, however, as already observed, proposed to alter the atomic weights in accordance with the periodic law of the elements, making Di = 138 (triad), Ce = 140, La = 180 (tetrads). But, according to recent determinations of the specific heats of these three metals, it would appear that in their most stable combinations they are all three triadic or trivalent. Hillebrand|| finds for the specific heats the following values:—

* Poggendorff's *Annalen*, xlv. 646; xlvii. 207; lvi. 511.

† From *exsiccation*, to be hid.

‡ From *διδυμοι*, twins.

|| Poggendorff's *Annalen* (1870), clxiii. 71.

| Ce | La | Di |
|---------|---------|---------|
| 0.04479 | 0.04485 | 0.04653 |

and Mendelejeff finds for cerium the number 0.050. Now, these numbers multiplied by the hitherto received atomic weights of the respective metals give for the atomic heats the values 4.12, 4.15, and 4.40, which do not agree with the law of Dulong and Petit (p. 225); but if these atomic weights are increased in the ratio of 2 to 3, which amounts to making their lower oxides sesquioxides, R_2O_3 , instead of monoxides, RO , their values, with small corrections, according to recent analyses by Hillebrand, become

| Ce | La | Di |
|-----|-----|---------|
| 138 | 139 | 144.75, |

giving for the atomic heats, the values

| | | |
|------|------|-------|
| 6.18 | 6.23 | 6.60, |
|------|------|-------|

which are in accordance with the general law.

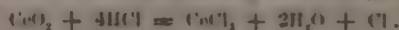
Cerium forms two series of compounds, viz., the cerous compounds, in which it is trivalent, as above stated, e. g., $CeCl_3$, Ce_2O_3 , $Ce_2(SO_4)_3$; and the ceric compounds, in which it is quadrivalent, e. g., ceric oxide, CeO_2 , [formerly ceroso-ceric oxide, Ce_2O_4], ceric sulphate, $Ce(SO_4)_2$,* etc. There are also two fluorine-compounds of cerium, in which it appears to have still higher equivalent values.

Cerous oxide, Ce_2O_3 , is obtained by igniting the carbonate or oxalate in a current of hydrogen, as a grayish-blue powder, quickly converted into ceric oxide on exposure to the air. Its salts are colorless. The *sulphate*, $Ce_2(SO_4)_3$, crystallizes with various quantities of water, according to the temperature at which it is deposited. *Cerium and potassium sulphate*, $CeK_3(SO_4)_3$, separates as a white powder on immersing solid potassium sulphate in a solution of a cerous salt. It is slightly soluble in pure water, but insoluble in a saturated solution of potassium sulphate. The formation of this salt affords the means of separating cerium from most other metals.

Ceric oxide, CeO_2 , is produced when cerous hydrate, carbonate, or nitrate is ignited in an open vessel. It is yellowish-white, acquires a deep orange-red color when heated, but recovers its original tint on cooling. It is not converted into a higher oxide by ignition in oxygen. *Ceric hydrate*, $2CeO_3 \cdot 3H_2O$, obtained by passing chlorine into aqueous potash in which cerous hydrate is suspended, is a bright yellow precipitate, which dissolves readily in sulphuric and nitric acids, forming yellow solutions of ceric salts; and in hydrochloric acid, with evolution of chlorine, forming colorless cerous chloride.

The solution of the sulphate yields by spontaneous evaporation, first, brown-red crystals of a *ceroso-ceric salt*, $\left. \begin{matrix} Ce_2(SO_4)_3 \\ 2Ce(SO_4)_2 \end{matrix} \right\} + 4Aq.$ and afterwards yellow indistinctly crystalline *ceric sulphate*, $Ce(SO_4)_2 \cdot 4Aq.$

All ceric compounds, when heated with hydrochloric acid, give off chlorine, and are reduced to the corresponding cerous compounds; thus, —



* If these formulae be doubled, the ceric compounds may also be regarded as containing trivalent cerium, e. g., Ce_2O_4 , or $\begin{matrix} O & - & Ce & - & O \\ | & & & & | \\ O & - & Ce & - & O \end{matrix}$

There is a *fluoride of cerium*, Ce_2F_6 (formerly CeF_3), which may be obtained as a yellow precipitate, and likewise occurs native as *fluocerite*, and an oxyfluoride, $\text{Ce}_2\text{F}_{10}\text{O}_2$, occurring as *fluocerine* at Finbo, in Sweden.

Lanthanum forms only one set of compounds, viz., LaCl_3 , La_2O_3 , $\text{La}_2(\text{SO}_4)_3$. There is, however, a higher oxide, the composition of which is not exactly known. Lanthanum salts are colorless; their solutions yield, with alkalis, a precipitate of *lanthanum hydroxide*, $\text{La}(\text{OH})_3$, which, when ignited, leaves the white anhydrous sesquioxide. Both the hydroxide and the anhydrous oxide dissolve easily in acids. *Lanthanum sulphate* forms small prismatic crystals, containing $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. *Lanthanum and potassium sulphate*, $\text{LaK}_2(\text{SO}_4)_3$, is formed, on mixing the solution of a lanthanum salt with potassium sulphate, as a white crystalline precipitate, resembling the corresponding cerium salt.

Didymium salts are rose-colored, and their solutions give, with alkalis, a pale rose-colored precipitate of the *hydroxide*, DiH_2O_3 , which, when ignited in a covered crucible, leaves the anhydrous monoxide, Di_2O_3 , in white, hard lumps. When, however, the hydroxide, nitrate, carbonate, or oxalate of didymium is heated in contact with the air, and not very strongly, a dark-brown peroxide is left, containing from 0.8 to 0.9 per cent. oxygen more than the monoxide. This, when treated with acids, dissolves readily, giving off oxygen and yielding a salt of the monoxide.

Didymium sulphate separates from an acid solution, by spontaneous evaporation, in well-defined rhombohedral crystals, exhibiting numerous secondary faces, and containing $\text{Di}_2(\text{SO}_4)_3 \cdot 8\text{Aq.}$; they are isomorphous with the similarly constituted sulphates of yttrium, and erbium. The sulphate is more soluble in cold than in hot water, and a solution saturated in the cold, deposits, when heated to the boiling-point, a crystalline powder containing $\text{Di}_2(\text{SO}_4)_3 \cdot 6\text{Aq.}$

Didymium and potassium sulphate, $\text{DiK}_2(\text{SO}_4)_3$, resembles the lanthanum salt.

Solutions of didymium salts exhibit a well-marked absorption spectrum,* containing two black lines inclosing a very bright space. One of these black lines is in the yellow, immediately following Fraunhofer's line D, the other is situated between E and b. These characters can be distinctly recognized in a solution half an inch deep, containing only 0.10 per cent. of didymium salt. Lanthanum salts do not exhibit an absorption spectrum.

YTTRIUM AND ERBIUM.

Y = 62. Eb = 168.9.

These metals exist as silicates in the gadolinite or ytterbite of Ytterby in Sweden, and in a few other rare minerals. A third metal, called terbium, has also been supposed to be associated with them; but recent experiments, especially those of Bahr and Bunsen,† have thrown very great doubt upon its existence.

To obtain the earths, yttria and erbia, in the separate state, gadolinite is digested with hydrochloric acid, and the solution separated from the silica is treated with oxalic acid, which throws down the oxalates of erbium and yttrium, together with those of calcium, cerium, lanthanum, and

* See LIGHT, p. 89.

† Ann. Ch. Pharm. cxxxvii. 1.

didymium. These oxalates are converted into nitrates; the solution is treated with excess of solid potassium sulphate, to separate the cerium metals; the erbium and yttrium, which still remain in solution, are again precipitated by oxalic acid; and the same treatment is repeated, till the solution of the mixed earths, when examined by the spectral apparatus, no longer exhibits the absorption-bands characteristic of didymium. To separate the erbia and yttria, they are again precipitated by oxalic acid. The oxalates are converted into nitrates, and the nitrates of erbium and yttrium are separated by a series of fractional crystallizations, the erbium salt being the less soluble of the two, and crystallizing out first; but the process requires attention to a number of details, which cannot be here described.*

Metallic erbium has not been isolated. Yttrium (containing erbium) was obtained by Berzelius, as a blackish-gray powder, by igniting yttrium chloride with potassium.

Yttrium and erbium have hitherto been regarded as dyads, with the atomic weights $Y = 61.7$, $Eb = 112.6$; but the close analogy of their compounds to those of lanthanum and didymium renders it more probable that they are triads, with the higher atomic weights above given. In the absence, however, of exact determinations of the specific heats of these metals, the question must for the present be regarded as undecided.

Erbia, Eb_2O_3 , obtained by ignition of erbium nitrate or oxalate, has a faint rose color. It does not melt at the strongest white heat, but aggregates to a spongy mass, glowing with an intense green light, which, when examined by the spectroscopic, exhibits a continuous spectrum intersected by a number of bright bands. Solutions of erbium-salts, on the other hand, give an absorption-spectrum exhibiting dark bands, and the points of maximum intensity of the light bands in the emission-spectrum of glowing erbia coincide exactly in position with the points of greatest darkness in the absorption spectrum. The position of these bands is totally different from those in the emission and absorption-spectra of didymium.†

Erbium salts have a rose-red color, deeper in the hydrated than in the anhydrous state; they have an acid reaction and sweet astringent taste. The sulphate, $Eb_2(SO_4)_3 \cdot 8Aq.$, forms light rose-colored crystals, isomorphous with the sulphates of yttrium and didymium.

Yttria, Y_2O_3 , is a soft, nearly white powder, which when ignited glows with a pure white light, and yields a spectrum not containing any bright bands, like that of erbia. It does not unite directly with water, but is precipitated as a hydrate by alkalis, from solutions of yttrium-salts. It dissolves slowly but completely in hydrochloric, nitric, and sulphuric acids, forming colorless solutions, which do not exhibit an absorption-spectrum.

Yttrium sulphate, $Y_2(SO_4)_3 \cdot 8Aq.$, forms small colorless crystals.

Reactions of the Earth-metals.

1. All these metals are precipitated from their solutions by ammonium sulphide, as hydrates, not as sulphides. They are not precipitated by hydrogen sulphide.

2. The hydrates of aluminium and beryllium are soluble in caustic potash; those of the other earth-metals are insoluble.

3. Beryllium hydrate dissolves in a cold saturated solution of ammonium carbonate, and is precipitated, as carbonate, on boiling. Aluminium hydrate is insoluble in ammonium carbonate (see further, p. 344).

* See Watts's Dictionary of Chemistry, vol. v. p. 721.

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4. Of the earth-metals whose hydrates are insoluble in potash,—namely, zirconium, thorium, cerium, lanthanum, didymium, erbium, and yttrium—zirconium and thorium may be precipitated as thiosulphates by boiling the solution with *sodium thiosulphate*, the other metals remaining in solution. The precipitate when ignited leaves pure zirconia and thorina, or a mixture of the two.

5. Zirconium and thorium may be separated one from the other by means of *ammonium oxalate*, which, when added in excess, precipitates the thorium as oxalate, and leaves the zirconium in solution.

6. Cerium, lanthanum, and didymium are separated from yttrium and erbium by adding an excess of *potassium sulphate*, which throws down the cerium metals, leaving yttrium and erbium in solution; to insure complete precipitation, the solution must be left in contact for some time with a piece of solid potassium sulphate.

Cerium may be separated from lanthanum and didymium, as already observed, by treating the mixed oxides several times with *nitric acid* (p. 347). Another method is to boil the mixed oxides (the cerium being in the state of ceric oxide) with solution of *sul-ammoniac*. The lanthanum and didymium then gradually dissolve, as chlorides, while the cerium remains as ceric oxide. A third method is to precipitate the solution of the three metals with excess of potash, and pass *chlorine* in excess through the solution and precipitate; the cerium is then separated as bright yellow ceric hydrate, while the lanthanum and didymium re-dissolve as chlorides. This reaction serves to detect very small quantities of cerium mixed with the other two metals. Cerium is further distinguished by the light-yellow color of anhydrous ceric oxide, and by the reaction of its compounds, when fused before the blowpipe with borax or phosphorus salt, the glass thus formed being deep red while hot, and becoming colorless on cooling. Didymium is distinguished by the dark-brown color of its higher oxide; by the pale rose-color which its salts impart to a bead of borax or phosphorus salt; and by the peculiar character of its absorption-spectrum (p. 349).

The methods of separating lanthanum from didymium, and yttrium from erbium—imperfect at the best—have been already noticed.

MANUFACTURE OF GLASS, PORCELAIN, AND EARTHEN-WARE.

Glass.—Glass is a mixture of various insoluble silicates with excess of silica, altogether destitute of crystalline structure; the simple silicates, formed by fusing the bases with silicic acid in equivalent proportions, very often crystallize, which happens also with the greater number of the natural silicates included among the earthy minerals. Compounds identical with some of these are also occasionally formed in artificial processes, where large masses of melted glassy matter are suffered to cool slowly. The alkaline silicates, when in a state of fusion, have the power of dissolving a large quantity of silica.

Two principal varieties of glass are met with in commerce, namely, glass composed of silica, alkali, and lime; and glass containing a large proportion of lead silicate: *crystal* and *plate glass* belong to the former division; *float glass*, and the material of artificial gems, to the latter. The lead promotes fusibility, and confers also density and lustre. Common green bottle-glass contains no lead, but much silicate of iron, derived from the impure materials. The principle of the glass manufacture is very simple. Silica in the shape of sand, is heated with potassium or sodium carbonate, and mixed lime or lead oxide; at a high temperature, fusion and combination occur, and the carbonic acid is expelled. Glauber's salt mixed

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with charcoal is sometimes substituted for soda. When the melted mass has become perfectly clear and free from air-bubbles, it is left to cool until it assumes the peculiar tenacious condition proper for working.

The operation of fusion is conducted in large crucibles of refractory fire-clay, which in the case of lead-glass are covered by a dome at the top, and have an opening at the side, by which the materials are introduced, and the melted glass withdrawn. Great care is exercised in the choice of the sand, which must be quite white and free from iron oxide. Red lead, one of the higher oxides, is preferred to litharge, although immediately reduced to monoxide by the heat, the liberated oxygen serving to destroy any combustible matter that might accidentally find its way into the crucible, and stain the glass by reducing a portion of the lead. Potash gives a better glass than soda, although the latter is very generally employed, from its lower price. A certain proportion of broken and waste glass of the same kind is always added to the other materials.

Articles of blown glass are thus made: The workman begins by collecting a proper quantity of soft pasty glass at the end of his *blowpipe*, an iron tube of five or six feet in length, terminated by a mouth-piece of wood; he then begins blowing, by which the lump is expanded into a kind of flask, susceptible of having its form modified by the position in which it is held, and the velocity of rotation continually given to the iron tube. If an open-mouthed vessel is to be made, an iron rod, called a *pontil* or *puntil*, is dipped into the glass pot and applied to the bottom of the flask, to which it thus serves as a handle, the blowpipe being removed by the application of a cold iron to the neck. The vessel is then reheated at a hole left for the purpose in the wall of the furnace, the aperture enlarged, and the vessel otherwise altered in figure by the aid of a few simple tools, until completed. It is then detached, and carried to the annealing oven, where it undergoes slow and gradual cooling during many hours, the object of which is to obviate the excessive brittleness always exhibited by glass which has been quickly cooled. The large circular *tables* of crown glass are made by a very curious process of this kind; the globular flask at first produced, transferred from the blowpipe to the pontil, is suddenly made to assume the form of a flat disk by the centrifugal force of the rapid rotatory movement given to the rod. Plate glass is cast upon a flat metal table, and, after very careful annealing, ground true and polished by suitable machinery. Tubes are made by rapidly drawing out a hollow cylinder; and from these a great variety of useful small apparatus may be constructed with the help of a lamp and blowpipe, or, still better, the bellows table of the barometer-maker. Small tubes may be bent in the flame of a spirit-lamp or gas-jet, and cut with great ease by a file, a scratch being made, and the two portions pulled or broken asunder in a way easily learned by a few trials.

Specimens of the two chief varieties of glass gave the following results on analysis:—

| Bohemian plate glass (excellent). | | English flint glass. | |
|-----------------------------------|------------|----------------------|-------------|
| Silica | 60.0 | Silica | 51.93 |
| Potassium oxide | 25.0 | Potassium oxide | 13.77 |
| Lead | 12.5 | Lead | 33.28 |
| | <hr/> 97.5 | | <hr/> 99.98 |

The difficultly fusible white Bohemian tube, so valuable in organic analysis, has been found to contain, in 100 parts—

| | |
|---|-------|
| Silica | 72.80 |
| Lime, with trace of alumina | 9.68 |
| Magnesia | .40 |
| Potassium oxide | 16.80 |
| Traces of manganese, etc., and loss | .32 |

Different colors are often communicated to glass by metallic oxides. Thus, oxide of cobalt gives deep blue; oxide of manganese, amethyst; cuprous oxide, ruby-red; cupric oxide, green; the oxides of iron, dull green or brown, etc. These are either added to the melted contents of the glass-pot, in which they dissolve, or applied in a particular manner to the surface of the plate or other object, which is then reheated, until fusion of the coloring matter occurs: such is the practice of enamelling and glass painting. An opaque white appearance is given by oxide of tin; the enamel of watch-faces is thus prepared.

Toughened Glass.—When ordinary glass is heated till it begins to soften, then plunged into melted paraffin, wax, or other substance melting at a comparatively low temperature, and then left to cool gradually, it becomes very tough, so that it may be struck or thrown on the ground without breaking. It has also acquired greater power of resisting heat, and may be heated to redness, then dipped into cold water, and whilst wet again held in the flame, without injury. Hence it is well adapted for lamp chimneys and for culinary vessels. When it does break, however, it splits up into a multitude of minute angular fragments, indicating a crystalline structure, the existence of which is confirmed by the appearance of the toughened glass in polarized light.

Soluble Glass.—When silica is melted with twice its weight of potassium or sodium carbonate, and the product treated with water, the greater part dissolves, yielding a solution from which acids precipitate gelatinous silica. This is *soluble glass* or *water glass*; its solution has been used for rendering muslin and other fabrics of cotton or linen less combustible, for making artificial stone, and preserving natural stones from decay, and for a peculiar style of mural painting called *stereochromy*.*

Porcelain and Earthenware.—The plasticity of natural clays, and their hardening when exposed to heat, are properties which suggested in very early times their application to the making of vessels for the various purposes of daily life: there are few branches of industry of higher antiquity than that exercised by the potter.

True porcelain is distinguished from earthenware by very obvious characters. In porcelain the body of the ware is very compact and translucent, and breaks with a conchoidal fracture, symptomatic of a commencement of fusion. The glaze, too, applied for giving a perfectly smooth surface, is closely adherent, and, in fact, graduates by insensible degrees into the substance of the body. In earthenware, on the contrary, the fracture is open and earthy, and the glaze detachable with greater or less facility. The compact and partly glassy character of porcelain is the result of the admixture with the clay of a small portion of some substance such as felspar, or a calcic or alkaline silicate, which is fusible at the temperature to which the ware is exposed when baked or fired, and being absorbed by the less fusible portion, binds the whole into a solid mass on cooling. The clay employed in porcelain-making is always directly derived from decomposed felspar, none of the clays of the secondary strata being pure enough for the purpose; it must be white, and free from iron oxide. To diminish the contraction which this substance undergoes in the fire, a quantity of finely divided silica, carefully prepared by crushing and grinding calcined flints

* See Richardson and Watt's *Chemical Technology*, vol. 1. part iv. pp. 69-104.

or chert, is added, together with a proper proportion of felspar or other fusible material, also reduced to impalpable powder. The utmost pains are taken to effect perfect uniformity of mixture, and to avoid the introduction of particles of grit, or other foreign bodies. The ware itself is fashioned either on the potter's wheel—a kind of vertical lathe—or in moulds of plaster of Paris, and dried first in the air, afterwards by artificial heat, and at length completely hardened by exposure to the temperature of ignition. The porous *biscuit* is now fit to receive its glaze, which may be either ground felspar, or a mixture of gypsum, silica, and a little porcelain clay, diffused through water. The piece is dipped for a moment into this mixture, and withdrawn; the water sinks into its substance, and the powder remains evenly spread upon its surface; it is once more dried, and, lastly, fired at an exceedingly high temperature.

The porcelain-furnace is a circular structure of masonry, having several fire-places, and surmounted by a lofty dome. Dry wood or coal is consumed as fuel, and its flame directed into the interior, and made to circulate around and among the earthen cases, or *seggars*, in which the articles to be fired are packed. Many hours are required for this operation, which must be very carefully managed. After the lapse of several days, when the furnace has completely cooled, the contents are removed in a finished state, so far as regards the ware.

The ornamental part, consisting of gilding and painting in enamel, has yet to be executed; after which the pieces are again heated, in order to flux the colors. The operation has sometimes to be repeated more than once.

The manufacture of porcelain in Europe is of modern origin: the Chinese have possessed the art from the commencement of the seventh century, and their ware is, in some respects, altogether unequalled. The materials employed by them are known to be *kaolin* or decomposed felspar; *petuntze*, or quartz reduced to fine powder; and the ashes of fern, which contain potassium carbonate.

Stoneware.—This is a coarse kind of porcelain, made from clay containing oxide of iron and a little lime, to which it owes its partial fusibility. The glazing is performed by throwing common salt into the heated furnace; this is volatilized, and decomposed by the joint agency of the silica of the ware and of the vapor of water always present; hydrochloric acid and soda are produced, the latter forming a silicate, which fuses over the surface of the ware, and gives a thin, but excellent glaze.

Earthenware.—The finest kind of earthenware is made from a white secondary clay, mixed with a considerable quantity of silica. The articles are thoroughly dried and fired; after which they are dipped into a readily fusible glaze mixture, of which lead oxide is usually an important ingredient, and, when dry, reheated to the point of fusion of the latter. The whole process is much easier of execution than the making of porcelain, and demands less care. The ornamental designs in blue and other colors, so common upon plates and household articles, are printed upon paper in enamel pigment mixed with oil, and transferred, while still wet, to the unglazed ware. When the ink becomes dry, the paper is washed off, and the glazing completed.

The coarser kinds of earthenware are sometimes covered with a whitish opaque glaze, which contains the oxides of lead and tin; such glaze is very liable to be attacked by acids, and is dangerous for culinary vessels.

Crucibles, when of good quality, are very valuable to the chemist. They are made of clay free from lime, mixed with sand or ground ware of the same description. The Hessian and Cornish crucibles are among the best. Sometimes a mixture of plumbago and clay is employed for the same purpose; and powdered coke has been also used with the earth: such crucibles bear rapid changes of temperature with impunity.

DYAD METALS.—GROUP II.

MAGNESIUM.

Atomic weight, 24. Symbol, Mg.

This metal was formerly classed with the metals of the alkaline earths, but it is much more nearly related to zinc by its properties in the free state, as well as by the volatility of its chloride, the solubility of its sulphate, and the isomorphism of several of its compounds with the analogously constituted compounds of zinc.

Magnesium occurs in the mineral kingdom as hydrate, carbonate, borate, phosphate, sulphate, and nitrate, sometimes in the solid state, sometimes dissolved in mineral waters: magnesian limestone, or dolomite, which forms entire mountain masses, is a carbonate of magnesium and calcium. Magnesium also occurs as silicate, combined with other silicates, in a variety of minerals, as steatite, hornblende, augite, talc, etc.; also as aluminate in spinelle and zeilanite. It likewise occurs in the bodies of plants and animals, chiefly as carbonate and phosphate, and in combination with organic acids.

Metallic magnesium is prepared:—

1. By the electrolysis of fused magnesium chloride, or, better, of a mixture of 4 molecules of magnesium chloride and 3 molecules of potassium chloride with a small quantity of sal-ammoniac. A convenient way of effecting the reduction is to fuse the mixture in a common clay tobacco-pipe over an Argand spirit-lamp or gas-burner, the negative pole being an iron wire passed up the pipe-stem, and the positive pole a piece of gas-pipe just touching the surface of the fused chlorides. On passing the current of a battery of ten Bunsen's cells through the arrangement, the magnesium collects round the extremity of the iron wire.

2. Magnesium may be prepared in much larger quantity by reducing magnesium chloride, or the double chloride of magnesium and sodium or potassium, with metallic sodium. The double chloride is prepared by dissolving magnesium carbonate in hydrochloric acid, adding an equivalent quantity of sodium or potassium chloride, evaporating to dryness, and fusing the residue. This product, heated with sodium in a wrought-iron crucible, yields metallic magnesium, containing certain impurities, from which it may be freed by distillation. This process is now carried out on the manufacturing scale, and the magnesium is drawn out into wire or rolled into ribband for burning.*

Magnesium is a brilliant metal, almost as white as silver, somewhat more brittle at common temperatures, but malleable at a heat a little below redness. Its specific gravity is 1.74. It melts at a red heat, and volatilizes at nearly the same temperature as zinc. It retains its lustre in dry air, but in moist air it becomes covered with a crust of magnesia.

Magnesium in the form of wire or ribband takes fire at a red heat, burning with a dazzling bluish-white light. The flame of a candle or spirit-lamp is sufficient to inflame it, but to insure continuous combustion, the metal must be kept in contact with the flame. For this purpose lamps are constructed, provided with a mechanism which continually pushes three or more magnesium wires into a small spirit-flame.

The magnesium flame produces a continuous spectrum, containing a very

* For details of the manufacturing process, see Richardson and Watts's *Chemical Technology*, vol. I. part v. pp. 346-352.

large proportion of the more refrangible rays : hence it is well adapted for photography, and has, indeed, been used for taking photographs, in the absence of the sun, or in places where sunlight cannot penetrate, as in caves or subterranean apartments.

Magnesium Chloride, $MgCl_2$.—When magnesia, or its carbonate, is dissolved in hydrochloric acid, magnesium chloride and water are produced ; but when this solution is evaporated to dryness, the last portions of water are retained with such obstinacy, that decomposition of the water is brought about by the concurring attractions of magnesium for oxygen, and of chlorine for hydrogen : hydrochloric acid is expelled, and magnesia remains. If, however, sal-ammoniac, potassium chloride, or sodium chloride is present, a double salt is produced, which is easily rendered anhydrous. The best mode of preparing the chloride is to divide a quantity of hydrochloric acid into two equal portions, to neutralize one with magnesia, and the other with ammonia, or carbonate of ammonia : to mix these solutions, evaporate them to dryness, and then expose the salt to a red heat in a loosely covered porcelain crucible. Sal-ammoniac sublimes, and magnesium chloride in a fused state remains ; the latter is poured out upon a clean stone, and when cold transferred to a well-stopped bottle.

The chloride so obtained is white and crystalline. It is very deliquescent and highly soluble in water, from which it cannot again be recovered by evaporation, for the reasons just mentioned. When long exposed to the air in the melted state, it is converted into magnesia. It is soluble in alcohol.

Magnesium Oxide, or Magnesia, MgO .—This oxide is easily prepared by exposing the *magnesia alba* of pharmacy, which is a hydrocarbonate, to a full red heat in an earthen or platinum crucible. It forms a soft, white powder, which slowly attracts moisture and carbonic acid from the air, and unites quietly with water to a hydrate which possesses a feeble degree of solubility, requiring about 5000 parts of water at $15.50^{\circ} C.$ ($60^{\circ} F.$) and 36,000 parts at $100^{\circ} C.$ ($212^{\circ} F.$). The alkalinity of magnesia can only be observed by placing a small portion in a moistened state upon test-paper : it neutralizes acids, however, in the most complete manner. It is infusible.

Magnesium sulphide is formed by passing vapor of carbon sulphide over magnesia, in capsules of coke, at a strong red heat.

Oxysalts of Magnesium.—The *sulphate*, $MgSO_4 \cdot 7H_2O$, commonly called Epsom salt, occurs in sea-water, and in many mineral springs, and is now manufactured in large quantities by acting on magnesian limestone with dilute sulphuric acid, and separating the magnesium sulphate from the greater part of the slightly soluble calcium sulphate by filtration. The crystals are derived from a right rhombic prism ; they are soluble in an equal weight of water at $5.5^{\circ} C.$ ($41.9^{\circ} F.$), and in a still smaller quantity at $100^{\circ} C.$ ($212^{\circ} F.$). The salt has a nauseous bitter taste, and, like many other neutral salts, possesses purgative properties. When it is exposed to heat, 6 molecules of water readily pass off, the seventh being energetically retained. Magnesium sulphate forms beautiful double salts with the sulphates of potassium and ammonium, which contain 6 molecules of crystallization-water, their formulas being $MgK_2(SO_4)_6 \cdot 6H_2O$, and $Mg(NH_4)_2(SO_4)_6 \cdot 6H_2O$. These salts are isomorphous, and form monoclinic crystals.

Carbonates.—The *neutral carbonate*, $MgCO_3$ or $MgO \cdot CO_2$, occurs native in rhombohedral crystals, resembling those of calc-spar, imbedded in talc-slate ; a soft earthy variety is sometimes met with.

When *magnesia alba* is dissolved in aqueous carbonic acid, and the so-

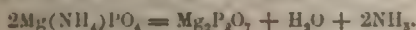
lation left to evaporate spontaneously, small prismatic crystals are deposited, consisting of trihydrated magnesium carbonate, $MgCO_3 \cdot 3H_2O$.

The magnesia alba itself, although often called carbonate of magnesium, is not so in reality; it is a compound of carbonate with hydrate. It is prepared by mixing hot solutions of potassium or sodium carbonate and magnesium sulphate, the latter being kept in slight excess, boiling the whole a few minutes, during which time much carbonic acid is disengaged, and well washing the precipitate so produced. If the solution is very dilute, the magnesia alba is exceedingly light and bulky; if otherwise, it is denser. The composition of this precipitate is not perfectly constant. In most cases it contains $4MgCO_3 \cdot MgH_2O_2 \cdot 6Aq$.

Magnesia alba is slightly soluble in water, especially when cold.

Magnesium phosphate, $MgHPO_4 \cdot 7H_2O$, separates in small colorless prismatic crystals when solutions of sodium phosphate and magnesium sulphate are mixed and suffered to stand for some time. According to Graham, it is soluble in about 1000 parts of cold water. Magnesium phosphate exists in the grain of the cereals, and can be detected in considerable quantity in beer.

Magnesium and Ammonium Phosphate, $Mg(NH_4)PO_4 \cdot 6H_2O$.—When ammonia or its carbonate is mixed with a magnesium salt, and a soluble phosphate is added, a crystalline precipitate, having the above composition, subsides, immediately if the solutions are concentrated, and after some time if very dilute: in the latter case, the precipitation is promoted by stirring. This salt is slightly soluble in pure water, but nearly insoluble in saline and ammoniacal liquids. When heated, it gives off water and ammonia, and is converted into *magnesium pyrophosphate*, $Mg_2P_2O_7$:



At a strong red heat it fuses to a white enamel-like mass. Magnesium and ammonium phosphate sometimes forms a urinary calculus, and occurs also in guano.

In analysis, magnesium is often separated from solutions by bringing it into this state. The liquid, free from alumina, lime, etc., is mixed with sodium phosphate and excess of ammonia, and gently heated for a short time. The precipitate is collected upon a filter and thoroughly washed with water containing a little ammonia, after which it is dried, ignited to redness, and weighed. The proportion of magnesia is then easily calculated.

Silicates.—The following natural compounds belong to this class: *Chrysolite*, $Mg_2SiO_4 = 2MgO \cdot SiO_2$, a crystallized mineral, sometimes employed for ornamental purposes: a portion of the magnesia is commonly replaced by ferrous oxide, which communicates a green color. *Meerschaum*, $2MgSiO_3 \cdot SiO_2 = 2MgO \cdot 3SiO_2$, is a soft sectile mineral, from which pipe-bowls are made. *Talc*, $4MgSiO_3 \cdot SiO_2 \cdot 4Aq$. (called *steatite* when massive), is a soft, white, sectile, transparent, or translucent mineral, used as firestones for furnaces and stoves, and in thin plates for glazing lanterns, etc.; also, in the state of powder for diminishing friction. *Soapstone*, also called *steatite*, is a silicate of magnesium and aluminium of somewhat variable composition. *Serpentine* is a combination of silicate and hydrate of magnesium. *Jade*, an exceedingly hard stone, brought from New Zealand, is a silicate of magnesium and aluminium: its green color is due to chromium. *Augite* and *basaltolende* are essentially double silicates of magnesia and lime, in which the magnesia is more or less replaced by its isomorphous substitute, ferrous oxide.

Magnesium salts are isomorphous with zinc salts, ferrous salts, cupric salts, cobalt salts, and nickel salts, etc.; they are usually colorless, and

are easily recognized by the following characters: A gelatinous white precipitate with *caustic alkalies*, including *ammonia*, insoluble in excess, but soluble in solution of sal-ammoniac. A white precipitate with *potassium* and *sodium carbonates*, but none with ammonium carbonate in the cold. A white crystalline precipitate with soluble *phosphates* on the addition of a little ammonia.

ZINC.

Atomic weight, 65.2. Symbol, Zn.

Zinc is a somewhat abundant metal: it is found in the state of carbonate, silicate and sulphide, associated with lead-ores in many districts, both in Britain and on the Continent; large supplies are obtained from Silesia, and from the neighborhood of Aachen. The native carbonate, or *calamine*, is the most valuable of the zinc ores, and is preferred for the extraction of the metal: it is first roasted to expel water and carbonic acid, then mixed with fragments of coke or charcoal, and distilled at a full red heat in a large earthen retort; carbon monoxide escapes, while the reduced metal volatilizes and is condensed by suitable means, generally with minute quantities of arsenic.

Zinc is a bluish-white metal, which slowly tarnishes in the air: it has a lamellar, crystalline structure, a density varying from 6.8 to 7.2, and is, under ordinary circumstances, brittle. Between 120° and 150° C. (248° and 302° F.) it is, on the contrary, malleable, and may be rolled or hammered without danger of fracture; and, what is very remarkable, after such treatment, it retains its malleability when cold; the sheet-zinc of commerce is thus made. At 210° C. (410° F.) it is so brittle that it may be reduced to powder. At 412° C. (773.6° F.) it melts; at a bright red heat it boils and volatilizes, and, if air be admitted, burns with a splendid greenish light, generating the oxide. Dilute acids dissolve zinc very readily: it is constantly employed in this manner for preparing hydrogen gas.

Zinc is a dyad metal, forming only one class of compounds.

The *chloride*, ZnCl_2 , may be prepared by heating metallic zinc in chlorine: by distilling a mixture of zinc-flings and corrosive sublimate; or, more easily, by dissolving zinc in hydrochloric acid. It is a nearly white, translucent, fusible substance, very soluble in water and alcohol, and very deliquescent. A strong solution of zinc chloride is sometimes used as a bath for obtaining a graduated heat above 100°. Zinc chloride unites with sal-ammoniac and potassium chloride to form double salts: the former of these, made by dissolving zinc in hydrochloric acid, and then adding an equivalent quantity of sal-ammoniac, is very useful in tinning and soft-soldering copper and iron.

The *oxide*, ZnO , is a strong base, forming salts isomorphous with the magnesium-salts. It is prepared either by burning zinc in atmospheric air, or by heating the carbonate to redness. Zinc oxide is a white, tasteless powder, insoluble in water, but freely dissolved by acids. When heated it is yellow, but turns white again on cooling. It is getting into use as a substitute for white lead. To prepare zinc-white on a large scale, metallic zinc is volatilized in large earthen muffles, whence the zinc vapor passes into a small receiver (*guêrite*), where it comes in contact with a current of air and is oxidized. The zinc oxide thus formed passes immediately into a condensing chamber divided into several compartments by *cloths suspended within it*.

The *sulphate*, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, commonly called *White Vitriol*.—This salt is easily to be distinguished by the eye from magnesium sulphate: it is prepared either by dissolving the metal in dilute sulphuric acid, or more economically, by roasting the native sulphide, or *blende*, which, by absorption of oxygen, becomes in great part converted into sulphate. The altered mineral is thrown hot into water, and the salt obtained by evaporating the clear solution. Zinc sulphate has an astringent metallic taste, and is used in medicine as an emetic. The crystals dissolve in $2\frac{1}{2}$ parts of cold, and in a much smaller quantity of hot, water. Crystals containing 6 molecules of water have been observed. Zinc sulphate forms double salts with the sulphates of potassium and ammonium, namely, $\text{ZnK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, isomorphous with the corresponding magnesium salts.

The *carbonate*, ZnCO_3 , is found native; the white precipitate obtained by mixing solutions of zinc and of alkaline carbonates, is a combination of carbonate and hydrate. When heated to redness, it yields pure zinc oxide.

The *sulphide*, ZnS , occurs native, as *blende*, in regular tetrahedrons, dodecahedrons, and other monometric forms, and of various colors, from white or yellow to brown or black, according to its degree of purity: it is a valuable ore of zinc. A variety, called *black jack*, occurs somewhat abundantly in Derbyshire, Cumberland, and Cornwall. A *hydrated sulphate*, $\text{ZnS} \cdot \text{H}_2\text{O}$, is obtained as a white precipitate on adding an alkaline sulphide to the solution of a zinc salt.

Zinc salts are distinguished by the following characters: *Caustic potash*, *soda*, and *ammonia*, give a white precipitate of hydrate, freely soluble in excess of the alkali. *Potassium* and *sodium carbonates* give white precipitates, insoluble in excess. *Ammonium carbonate* gives also a white precipitate, which is redissolved by an excess. *Potassium ferrocyanide* gives a white precipitate. *Hydrogen sulphide* causes no change in zinc solutions containing free mineral acids; but in neutral solutions, or with zinc salts of organic acids, such as the acetate, a white precipitate is formed. *Ammoniacal sulphide* throws down white sulphide of zinc, insoluble in caustic alkalis. The formation of this precipitate in a solution containing excess of caustic alkali, serves to distinguish zinc from all other metals.

All zinc compounds, heated on charcoal with sodium carbonate in the inner blow-pipe flame, give an incrustation of zinc oxide, which is yellow while hot, but becomes white in cooling. If this incrustation be moistened with a dilute solution of cobalt nitrate, and strongly heated in the outer flame, a fine green color is produced.

The applications of metallic zinc to the purposes of roofing, the construction of water channels, etc., are well known; it is sufficiently durable, but inferior in this respect to copper. It is much used also for protecting iron and copper from oxidation when immersed in saline solutions, such as sea-water, or exposed to damp air. This it does by forming an electric circuit, in which it acts as the positive or more oxidable metal (p. 257). *Galvanized iron* consists of iron having its surface coated with zinc.

CADMIUM.

Atomic weight, 112. Symbol, Cd.

This metal was discovered in 1817 by Stromeyer, and by Hermann: it accompanies the ores of zinc, especially those occurring in Silesia, and,

being more volatile than that substance, rises first in vapor when the calamine is subjected to distillation with charcoal. Cadmium resembles tin in color, but is somewhat harder; it is very malleable, has a density of 8.7, melts below 200° , and is nearly as volatile as mercury. It tarnishes but little in the air, but burns when strongly heated. Dilute sulphuric and hydrochloric acids act but little on cadmium in the cold; nitric acid is its best solvent.

The observed vapor-density of cadmium is 3.94 compared with air, or 56.3 compared with hydrogen, which latter number does not differ greatly from the half of 112, the atomic weight of the metal: hence it appears that the atom of cadmium in the state of vapor occupies twice the space of an atom of hydrogen (p. 228).

Cadmium, like zinc, is dyadic, and forms but one series of compounds. The oxide, CdO , may be prepared by igniting either the carbonate or the nitrate: in the former case it has a pale-brown color, and in the latter a much darker tint, and forms octohedral microscopic crystals. Cadmium oxide is infusible: it dissolves in acids, producing a series of colorless salts: it attracts carbonic acid from the air, and turns white. The sulphate, $\text{CdSO}_4 \cdot 4\text{H}_2\text{O}$, is easily obtained by dissolving the oxide or carbonate in dilute sulphuric acid: it is very soluble in water, and forms double salts with the sulphates of potassium and ammonium, which contain respectively $\text{CdK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The chloride, CdCl_2 , is a very soluble salt, crystallizing in small four-sided prisms. The sulphide, CdS , is a very characteristic compound, of a bright yellow color, forming microscopic crystals, fusible at a high temperature. It is obtained by passing sulphuretted hydrogen gas through a solution of the sulphate, nitrate, or chloride. This compound is used as a yellow pigment, of great beauty and permanence. It occurs native as *greenockite*.

Fixed caustic *alkalies* give with cadmium salts a white precipitate of hydrated oxide, insoluble in excess. *Ammonia* gives a similar white precipitate, readily soluble in excess. The *fixed alkaline carbonates*, and *ammonia carbonate*, throw down white cadmium carbonate, insoluble in excess of either precipitant. *Hydrogen sulphide* and *ammonium sulphide* precipitate the yellow sulphide of cadmium.

GROUP III.

COPPER.

Atomic weight, 63.4. Symbol, Cu (Cuprum).

COPPER is a metal of great value in the arts: it sometimes occurs in the metallic state, crystallized in octohedrons, or more frequently in dodecahedrons, but is more abundant in the form of red oxide, and in that of sulphide combined with sulphide of iron, as *yellow copper ore* or *copper pyrites*. Large quantities of the latter substance are annually obtained from the Cornish mines, and taken to South Wales for reduction, which is effected by a somewhat complex process. The principle of this may, however, be easily made intelligible. The ore is roasted in a *reverberatory furnace*, by which much of the iron sulphide is converted into oxide,

while the copper sulphide remains unaltered. The product of this operation is then strongly heated with silicious sand; the latter combines with the iron oxide to a fusible *slag*, and separates from the heavier copper compound. When the iron has, by a repetition of these processes, been got rid of, the copper sulphide begins to decompose in the flame-furnace, losing its sulphur and absorbing oxygen; the temperature is then raised sufficiently to reduce the oxide thus produced, by the aid of carbonaceous matter. The last part of the operation consists in thrusting into the melted metal a pole of birch-wood, the object of which is probably to reduce a little remaining oxide by the combustible gases thus generated. Large quantities of extremely valuable ore, chiefly carbonate and red oxide, have lately been obtained from South Australia and Chile.

Copper has a well-known yellowish-red color, a specific gravity of 8.96, and is very malleable and ductile: it is an excellent conductor of heat and electricity: it melts at a bright red heat, and seems to be slightly volatile at a very high temperature. Copper undergoes no change in dry air; exposed to a moist atmosphere, it becomes covered with a strongly adherent green crust, consisting in a great measure of carbonate. Heated to redness in the air, it is quickly oxidized, becoming covered with a black scale. Dilute sulphuric and hydrochloric acids scarcely act upon copper; boiling oil of vitriol attacks it, with evolution of sulphurous oxide; nitric acid, even dilute, dissolves it readily, with evolution of nitrogen dioxide.

Copper, in its most stable compounds, the cupric compounds, is bivalent, these compounds containing 1 atom of the metal combined with 2 atoms of a univalent, or 1 atom of a bivalent negative radicle, e. g., CuCl_2 , CuO , $\text{Cu}(\text{NO}_3)_2$, CuSO_4 , etc. It also forms another series, the cuprous compounds, in which it may be regarded as univalent, e. g., CuCl , Cu_2O , etc., like silver in the argentic compounds. On the other hand, the cuprous compounds may be supposed to be formed by addition of copper to the cupric compounds, the metal still remaining bivalent, thus, cuprous chlor-

ide, $\text{Cu}_2\text{Cl}_2 = \begin{array}{c} \text{CuCl} \\ | \\ \text{CuCl} \end{array}$; cuprous oxide, $\text{Cu}_2\text{O} = \begin{array}{c} \text{Cu} \\ | \quad \diagup \quad \diagdown \\ \text{Cu} \quad \text{O} \end{array}$. These com-

pounds are very unstable, being easily converted into cupric compounds by the action of oxidizing agents.

Copper Chlorides.—*Cupric chloride*, CuCl_2 , is most easily prepared by dissolving cupric oxide in hydrochloric acid, and concentrating the green solution thence resulting. It forms green crystals, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, very soluble in water and in alcohol: it colors the flame of the latter green. When gently heated, it parts with its water of crystallization and becomes yellowish-brown; at a high temperature, it loses half its chlorine, and becomes converted into *cuprous chloride*. The latter is a white, fusible substance, but little soluble in water, and prone to oxidation: it is formed when copper-filings or copper-leaf are put into chlorine gas; also, by precipitating a solution of cupric chloride or other cupric salt with stannous chloride.—



A plate of copper immersed in hydrochloric acid in a vessel containing air becomes covered with white tetrahedrons of cuprous chloride. This compound dissolves in hydrochloric acid, forming a colorless solution, which gradually turns blue on exposure to the air.

A hydrated cupric oxychloride, $\text{CuCl}_2 \cdot 3\text{CuH}_2\text{O}_2$, occurs native as *atacamite*.

Both the chlorides of copper form double salts with the chlorides of the alkali-metals.

Cuprous Hydride, Cu_2H_2 .—When a solution of cupric sulphate is heated to about 70° , with hypophosphorous acid, this compound is deposited as a yellow precipitate, which soon turns red-brown. It gives off hydrogen when heated, takes fire in chlorine gas, and is converted by hydrochloric acid into cuprous chloride, with evolution of a double quantity of hydrogen, the acid giving up its hydrogen as well as the copper hydride:—



This reaction affords a remarkable instance of the union of two atoms of the same element to form a molecule (see page 234).

Copper Oxides.—Two oxides of copper are known, corresponding with the chlorides; and a very unstable dioxide or peroxide, CuO_2 , is said to be formed, as a yellowish-brown powder, by the action of hydrogen dioxide on cupric hydrate.

Copper Monoxide, Cupric Oxide, or Black Oxide of Copper, CuO , is prepared by calcining metallic copper at a red heat, with full exposure to air, or, more conveniently, by heating the nitrate to redness, which then suffers complete decomposition. Cupric salts mixed with caustic alkali in excess yield a bulky pale-blue precipitate of hydrated cupric oxide, or cupric hydrate, $\text{Cu}(\text{OH})_2$ or $\text{CuO} \cdot \text{H}_2\text{O}$, which, when the whole is raised to the boiling point, becomes converted into a heavy dark-brown powder: this also is anhydrous oxide of copper, the hydrate suffering decomposition, even in contact with water. The oxide prepared at a high temperature is perfectly black and very dense. Cupric oxide is soluble in acids, and forms a series of very important salts, isomorphous with magnesium salts.

Cuprous Oxide, Cu_2O , also called *Red Oxide* and *Suboxide of Copper*.—This oxide may be obtained by heating in a covered crucible a mixture of 5 parts of black oxide and 4 parts of fine copper filings; or by adding grape sugar to a solution of cupric sulphate, and then putting in an excess of caustic potash; the blue solution, heated to ebullition, is reduced by the sugar, and deposits cuprous oxide. This oxide often occurs in beautiful transparent ruby-red crystals, associated with other ores of copper, and can be obtained in the same state by artificial means. It communicates to glass a magnificent red tint, while that given by cupric oxide is green.

Cuprous oxide dissolves in excess of hydrochloric acid, forming a solution of cuprous chloride, from which that compound is precipitated on dilution with water. Most oxygen acids, namely, sulphuric, phosphoric, acetic, oxalic, tartaric, and citric acids, decompose cuprous oxide, forming cupric salts, and separating metallic copper; nitric acid converts it into cupric nitrate. Hence, there are but few cuprous oxygen-salts, none, indeed, excepting the sulphites, and certain double sulphites formed by mixing a cupric solution with the sulphite of an alkali-metal, e. g., ammonio-cuprous sulphite, $\text{Cu}(\text{NH}_4)\text{SO}_3$, or $\text{Cu}_2(\text{NH}_4)_2(\text{SO}_3)_2$.

Cupric Oxysalts.—The *sulphate*, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, commonly called *blue vitriol*, is prepared by dissolving cupric oxide in sulphuric acid, or, at less expense, by oxidizing the sulphide. It forms large blue triclinic prisms, soluble in four parts of cold and two parts of boiling water; when heated to 100° it readily loses four molecules of crystallization-water, but the fifth is retained with great pertinacity, and is expelled only at a low red heat. At a very high temperature, cupric sulphate is entirely converted into cupric oxide, with evolution of sulphurous oxide and oxygen. Cupric sulphate combines with the sulphates of potassium and of ammonium, forming pale-blue salts, $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, isomorphous with the corresponding magnesium salts.

Cupric Nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, is easily made by dissolving the metal in nitric acid; it forms deep blue crystals, very soluble and deliquescent. It is highly corrosive. An insoluble basic nitrate is known; it is green.

Cupric Carbonate.—When sodium carbonate is added in excess to a solution of cupric sulphate, the precipitate is at first pale-blue and flocculent, but by warming it becomes sandy, and assumes a green tint; in this state it contains $\text{CuCO}_3 \cdot \text{CuH}_2\text{O}_2 + \text{Aq.}$ This substance is prepared as a pigment. The beautiful mineral *malachite* has a similar composition, but contains no water of crystallization, its composition being $\text{CuCO}_3 \cdot \text{CuH}_2\text{O}_2$. Another natural compound, called *azurite*, not yet artificially imitated, occurs in large transparent crystals of the most intense blue: it contains $2\text{Cu}(\text{CO}_3) \cdot \text{CuH}_2(\text{O})_2$. *Verditer*, made by decomposing cupric nitrate with chalk, is said, however, to have a somewhat similar composition.

Cupric Arsenite is a bright green insoluble powder, prepared by mixing the solutions of a cupric salt with an alkaline arsenite.

COPPER SULPHIDES.—There are two well-defined copper sulphides, analogous in composition to the oxides, and four others, containing larger proportions of sulphur, but of less defined constitution; these latter are precipitated from solutions of cupric salts by potassium pentasulphide.

Cupric Sulphide, CuS , occurs native as *indigo copper* or *corallin*, in soft bluish black hexagonal plates and spheroidal masses, and is produced artificially by precipitating cupric salts with hydrogen sulphide.

Cuprous Sulphide, Cu_2S , occurs native as *copper-glance* or *redanthite*, in lead-gray hexagonal prisms, belonging to the rhombic system; it is produced artificially by the combustion of copper-foil in sulphur vapor, by igniting cupric oxide with sulphur, and by other methods. It is a powerful sulphur-base, uniting with the sulphides of antimony, arsenic, and bismuth, to form several natural minerals. The several varieties of *fahl-ore*, or *tetrahedrite*, consist of cuprous sulphantimonite or sulpharsenite, in which the copper is more or less replaced by equivalent quantities of iron, zinc, silver, and mercury. The important ore, called *copper-pyrites*, is a cuproso-ferric sulphide, $\text{Cu}(\text{Fe}^{II})\text{S}_2$ or $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$, occurring in tetrahedral crystals of the quadratic system, or in irregular masses. Another species of copper and iron sulphide, containing various proportions of the two metals, occurs native, as *purple copper* or *erubescite*, in cubes, octohedrons, and other monometric forms.

Ammoniacal Copper-compounds.—The chlorides, sulphate, nitrate, and other salts of copper, unite with one or more molecules of ammonia, forming, for the most part, crystalline compounds of blue or green color, some of which may be regarded as salts of metallammoniums (p. 349). Thus cupric chloride forms with ammonia, the compounds, $2\text{NH}_3 \cdot \text{CuCl}_2$, $4\text{NH}_3 \cdot \text{CuCl}_2$, and $6\text{NH}_3 \cdot \text{CuCl}_2$, the first of which may be formulated as *cupro-diammonium chloride*, $(\text{N}_2\text{H}_6\text{Cu}^{II})\text{Cl}_2$. Cupric sulphate forms, in like manner, *cupro-diammonium sulphate* $(\text{N}_2\text{H}_6\text{Cu}^{II})\text{SO}_4$, which is a deep blue crystalline salt. Cuprous iodide forms with ammonia the compound, $4\text{NH}_3 \cdot \text{Cu}_2\text{I}_2$.

Caustic potash gives with cupric salts a pale blue precipitate of cupric hydrate, changing to blackish-brown anhydrous oxide on boiling.—*Ammonia* also throws down the hydrate; but, when in excess, redissolves it, yielding a deep purplish-blue solution.—*Potassium* and *sodium carbonates* give pale blue precipitates of cupric carbonate, insoluble in excess.—*Ammonium carbonate* the same, but soluble with deep blue color.—*Potassium ferrocyanide* gives a fine red-brown precipitate of cupric ferrocyanide.—

Hydrogen sulphide and ammonium sulphide afford black cupric sulphide, insoluble in ammonium sulphide.

The alloys of copper are of great importance. *Brass* consists of copper alloyed with from 28 to 34 per cent. of zinc; the latter may be added directly to the melted copper, or granulated copper may be heated with calamine and charcoal-powder, as in the old process. *Gun-metal*, a most valuable alloy, consists of 90 parts copper and 10 tin. *Bell and speculum metal* contain a still larger proportion of tin; these are brittle, especially the last named. A good bronze for statues is made of 91 parts copper, 2 parts tin, 6 parts zinc, and 1 part lead. The *brass* or *bronze* of the ancients is an alloy of copper with tin, often also containing lead, and sometimes zinc.

MERCURY.

Atomic weight, 200. Symbol, Hg (Hydrargyrum).

This very remarkable metal, sometimes called *quicksilver*, has been known from early times, and perhaps more than all others has excited the attention and curiosity of experimenters, by reason of its peculiar physical properties. Mercury is of great importance in several of the arts, and enters into the composition of many valuable medicines.

Metallic mercury is occasionally met with in globules disseminated through the native sulphide, which is the ordinary ore. This latter substance, sometimes called *cinnabar*, is found in considerable quantity in several localities, of which the most celebrated are Almaden in Spain, and Idria in Austria. Only recently it has been discovered in great abundance, and of remarkable purity, in California and Australia. The metal is obtained by heating the sulphide in an iron retort with lime or scraps of iron, or by roasting it in a furnace, and conducting the vapors into a large chamber, where the mercury is condensed, while the sulphurous acid is allowed to escape. Mercury is imported into this country in bottles of hammered iron, containing seventy-five pounds each, and in a state of considerable purity. When purchased in smaller quantities, it is sometimes found adulterated with tin and lead, which metals it dissolves to some extent without much loss of fluidity. Such admixture may be known by the foul surface the mercury exhibits when shaken in a bottle containing air, and by the globules, when made to roll upon the table, leaving a train or tail.

Mercury has a nearly silver-white color, and a very high degree of lustre: it is liquid at all ordinary temperatures, and solidifies only when cooled to -40° . In this state it is soft and malleable. At 350° C. (662° F.) it boils, and yields a transparent, colorless vapor, of great density. The metal volatilizes, however, to a sensible extent at all temperatures above 19° or 21° C. (66.20° or 69.80° F.); below this point its volatility is imperceptible. The volatility of mercury at the boiling heat is much retarded by the presence of minute quantities of lead or zinc. The specific gravity of mercury at 15.5° C. (60° F.) is 13.59; that of frozen mercury about 14, great contraction taking place in the act of solidification.

Pure mercury is quite unalterable in the air at common temperatures, but when heated to near its boiling point, it slowly absorbs oxygen, and becomes converted into a crystalline dark-red powder, which is the highest

oxide. At a dull red heat this oxide is again decomposed into its constituents. Hydrochloric acid has little or no action on mercury, and the same may be said of sulphuric acid in a diluted state: when the latter is concentrated and boiling hot, it oxidizes the metal, converting it into mercuric sulphate, with evolution of sulphurous oxide. Nitric acid, even dilute and in the cold, dissolves mercury freely, with evolution of nitrogen dioxide.

The observed vapor-density of mercury referred to air as unity is 6.7; this referred to hydrogen is nearly 100;* that is to say, half the atomic weight of the metal: consequently the atom of mercury, like that of cadmium, occupies in the gaseous state twice the volume of an atom of hydrogen (see page 228).

Mercury forms two series of compounds, namely, the mercuric compounds, in which it is bivalent, as HgCl_2 , HgO , HgSO_4 , etc., and the mercurous compounds, in which it is apparently univalent, as Hg_2Cl_2 , Hg_2O , etc. These compounds are analogous in constitution to the cupric and cuprous compounds; and the mercurous compounds, like the latter, are easily converted into mercuric compounds by the action of oxidizing agents, which remove one atom of mercury; but they are, on the whole, much more stable than the cuprous compounds.

Mercury Chlorides.—*Mercuric chloride*, HgCl_2 , commonly called *Corrosive Sublimate*.—This compound may be obtained by several different processes: (1) When metallic mercury is heated in chlorine gas, it takes fire and burns, producing this substance. (2) It may be made by dissolving mercuric oxide in hot hydrochloric acid, crystals of corrosive sublimate then separating on cooling. (3) Or, more economically, by subliming a mixture of equal parts of mercuric sulphate and dry common salt, and this is the plan generally followed. The decomposition is represented by the equation:—



Sublimed mercuric chloride forms a white transparent crystalline mass, of specific gravity 5.43; it melts at 265°C . (509°F .), boils at 295°C . (563°F .), and volatilizes somewhat more easily than calomel, even at ordinary temperatures. Its observed vapor-density, referred to hydrogen as unity, is 140: and the density calculated from the formula HgCl_2 , supposing that the molecule occupies the same space as a molecule or two

atoms of hydrogen, p. 228, is $\frac{200 + 2 \times 35.5}{2} = 135.5$; the near agreement of this number with the observed result shows that the vapor is in the normal state of condensation.

Mercuric chloride dissolves in 16 parts of cold and 3 parts of boiling water, and crystallizes from a hot solution in long white prisms. Alcohol and ether also dissolve it with facility; the latter even withdraws it from a watery solution.

Mercuric chloride combines with a great number of other metallic chlorides, forming a series of beautiful double salts, of which the ancient *sal decaeseth* may be taken as a good example: it contains $\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$. *Corrosive sublimate* absorbs ammoniacal gas with great avidity, generating the compound $\text{HgCl}_2 \cdot \text{NH}_3$.

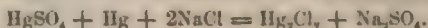
Mercuric chloride forms several compounds with mercuric oxide. These are produced by several processes, as when an alkaline carbonate is added in varying proportions to a solution of mercuric chloride. They differ

* $\frac{6.7}{0.0672} = 98.3$.
31*

greatly in color and physical character, and are mostly decomposed by water.

Mercuric chloride forms insoluble compounds with many of the azotized organic principles, as albumin, etc. It is perhaps to this property that its strong antiseptic properties are due. Animal and vegetable substances are preserved by it from decay, as in Kyan's method of preserving timber and cordage. Albumin is on this account an excellent antidote to corrosive sublimate in cases of poisoning.

Mercurous Chloride, Hg_2Cl_2 , commonly called *Calomel*. This very important substance may be easily and well prepared by pouring a solution of mercurous nitrate into a large excess of dilute solution of common salt. It falls as a dense white precipitate, quite insoluble in water; it must be thoroughly washed with boiling distilled water, and dried. Calomel is, however, generally procured by another and more complex process. Dry mercuric sulphate is rubbed in a mortar with as much metallic mercury as it already contains, and a quantity of common salt, until the globules disappear, and an uniform mixture has been produced. This is subjected to sublimation, and the vapor of the calomel, being carried into an atmosphere of steam, or into a chamber containing air, is thus condensed in a minutely divided state, and the laborious process of pulverization of the sublimed mass is avoided. The reaction is thus explained:



Pure calomel is a heavy, white, insoluble tasteless powder: it rises in vapor at a temperature below redness, and is obtained by ordinary sublimation as a yellowish-white crystalline mass. It is as insoluble in cold dilute nitric acid as silver chloride; boiling-hot strong nitric acid oxidizes and dissolves it. Calomel is instantly decomposed by an alkali, or by lime-water, with production of mercurous oxide. It is sometimes apt to contain a little mercuric chloride, which would be a very dangerous contamination in calomel employed for medical purposes. This is easily discovered by boiling with water, filtering the liquid, and adding caustic potash. Any corrosive sublimate is indicated by a yellow precipitate.

The observed vapor-density of calomel referred to hydrogen as unity, is 119.2. Now the formula Hg_2Cl_2 , if it represents a molecule occupying in the gaseous state two volumes (i. e., twice the volume of an atom of hydrogen, p. 228), would give a density nearly double of this: for

$$\frac{400 + 2 \times 35.5}{2} = 235.5.$$

Hence it might be inferred that the composition of calomel should rather be represented by the simpler formula HgCl , which would give for the vapor-density the number 117.75. The frequent decomposition of mercurous salts into mercuric salts and free mercury is however in favor of the supposition that their molecules contain two atoms of mercury: and the anomaly in the vapor-volume of calomel may be explained by supposing that the vapor of this compound, like that of many others, undergoes at high temperatures the change known as *dissociation* (p. 230), the two volumes of mercurous chloride, Hg_2Cl_2 , being resolved into two volumes of mercuric chloride, HgCl_2 , and two volumes of mercury, Hg . This supposition is, to some extent, warranted by the observation that calomel vapor amalgamates gold-leaf, and that corrosive sublimate may be detected in resublimed calomel.

Iodides.—Mercuric iodide, HgI_2 , is formed, when solution of potassium iodide is mixed with mercuric chloride, as a precipitate which is at first

yellow, but in a few moments changes to a most brilliant scarlet, this color being retained on drying. This is the neutral iodide: it may be made, although of rather duller tint, by triturating equivalent quantities of iodine and mercury with a little alcohol. In preparing it by precipitation, it is better to weigh out the proper proportions of the two salts, as the iodide is soluble in an excess of either, more especially in excess of potassium iodide. Mercuric iodide exhibits a very remarkable case of dimorphism, attended with difference of color, which is red or yellow, according to the figure assumed. Thus, when the iodide is suddenly exposed to a high temperature, it becomes bright yellow throughout, and yields a copious sublimate of minute but brilliant yellow crystals. If in this state it be touched by a hard body, it instantly becomes red, and the same change happens spontaneously after a certain lapse of time. On the other hand, by a very slow and careful heating, a sublimate of red crystals, having a totally different form, may be obtained, which are permanent. The same kind of change happens with the freshly precipitated iodide, the yellow crystals first formed breaking up in a few seconds, from the passage of the salt to the red modification.

Mercuric iodide forms double salts with the more basic or positive metallic iodides, as those of the alkali-metals and alkaline earth-metals; thus it dissolves in aqueous potassium-iodide, and the hot solution deposits, on cooling, crystals of potassio-mercuric iodide, $2(KI.HgI_2).3H_2O$. They are decomposed by water, with separation of about half the mercuric iodide, the solution then containing the salt, $2KI.HgI_2$, which remains as a saline mass on evaporation.

Mercurous Iodide, Hg_2I_2 , is formed when a solution of potassium iodide is added to mercurous nitrate: it then separates as a dirty yellow, insoluble precipitate, with a tinge of green. It may also be prepared by rubbing mercury and iodine together in a mortar in the proportion of 1 atom of the former to 1 atom of the latter, the mixture being moistened from time to time with alcohol.

Oxides.—*Monoxide, or Mercuric Oxide*, HgO , commonly called *Red Oxide of Mercury*, or *Red Precipitate*.—There are numerous methods by which this compound may be obtained. The following may be cited as the most important: (1) By exposing mercury in a glass flask with a long narrow neck, for several weeks, to a temperature approaching $315^{\circ} C.$ ($600^{\circ} F.$). The product has a dark red color, and is highly crystalline; it is the *red precipitate* of the old writers. (2) By cautiously heating any of the mercuric or mercurous nitrates to complete decomposition, whereby the acid is decomposed and expelled, oxidizing the metal to a maximum, if it happens to be in the state of mercurous salt. The product thus obtained is also crystalline and very dense, but has a much paler color than the preceding; while hot, it is nearly black. It is by this method that the oxide is generally prepared; it is apt to contain undecomposed nitrate, which may be discovered by strongly heating a portion in a test-tube: if red fumes are produced, or the odor of nitrous acid exhaled, the oxide has been insufficiently heated in the process of manufacture. (3) By adding caustic potash in excess to a solution of corrosive sublimate, by which a bright yellow precipitate of mercuric oxide is thrown down, which differs from the foregoing preparations merely in being destitute of crystalline texture and much more minutely divided. It must be well washed and dried.

Mercuric oxide is slightly soluble in water, communicating to the latter an alkaline reaction and metallic taste: it is highly poisonous. When strongly heated, it is decomposed, as before observed, into metallic mercury and oxygen gas.

only mercurous salts, and these are neutral or basic—i. e., oxy (p. 286)—as the acid or the metal happens to be in excess. When, contrary, the nitric acid is concentrated and hot, the mercury is in its highest state of oxidation, and a mercuric salt is produced; classes of salts are apt to be decomposed by a large quantity of giving rise to insoluble, or sparingly soluble, basic compounds.

Mercuric Nitrates.—By dissolving mercuric oxide in excess of nitric acid and evaporating gently, a syrupy liquid is obtained, which, in a bell-jar over lime or sulphuric acid, deposits bulky crystals and fine crusts, both having the composition $2\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. The substance is deposited from the syrupy liquid as a crystalline powder dropping it into concentrated nitric acid. The syrupy liquid itself is to be a definite compound, containing $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. By saturating dilute nitric acid with mercuric oxide, a salt is obtained on cooling crystallizes in needles, permanent in the air, containing $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. The preceding crystallized salts are decomposed by water, with production of compounds more and more basic as the washing is prolonged, temperature of the water raised.

Mercurous Nitrate, $(\text{Hg}_2)(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, forms large colorless crystals in a small quantity of water without decomposition; it is made by dissolving mercury in an excess of cold dilute nitric acid.

When excess of mercury has been employed, a finely crystallized salt is deposited after some time, containing $(\text{Hg}_2)(\text{NO}_3)_2 \cdot 2\text{Hg}_2\text{O} \cdot 3\text{H}_2\text{O} \cdot \text{N}_2\text{O}_5$; this is also decomposed by water. The two salts are easily distinguished when rubbed in a mortar with a little sodium chloride; the neutral compound gives sodium nitrate and calomel; the basic sodium nitrate and a black compound of calomel with mercurous chloride. A black substance, called *Hahnemann's soluble mercury*, is produced when ammonia in small quantity is dropped into a solution of mercurous nitrate; it contains $2\text{NH}_3 \cdot 3\text{Hg}_2\text{O} \cdot \text{N}_2\text{O}_5$, or, according to Kane, $2\text{NH}_3 \cdot 2\text{Hg}_2\text{O} \cdot \text{N}_2\text{O}_5$; composition of this preparation evidently varies according to the temperature and the concentration of the solutions.

Mercury Sulphates.—**Mercuric Sulphate**, HgSO_4 , is readily prepared by boiling together oil of vitriol and metallic mercury until the H

Mercury Sulphides.—*Mercuric Sulphide*, HgS , occurs native as cinnabar a dull-red mineral, which is the most important ore of mercury. Hydrogen sulphide passed in small quantity into a solution of mercuric nitrate, or chloride, forms a white precipitate, which is a compound of mercuric sulphide with the salt itself. An excess of the gas converts the whole into sulphide, the color at the same time changing to black. When this black sulphide is sublimed, it becomes dark-red and crystalline, but undergoes no change of composition: it is then cinnabar or vermillion. Mercuric sulphide is most easily prepared by subliming an intimate mixture of 5 parts of mercury and 1 part of sulphur, and reducing the resulting cinnabar to very fine powder, the beauty of the tint depending much upon the extent to which division is carried. The red or crystalline sulphide may also be formed directly, without sublimation, by heating the black precipitated substance in a solution of potassium pentasulphide; the mercuric sulphide is, in fact, soluble to a certain extent, in the alkaline sulphides, and forms with them crystallizable compounds.

When vermillion is heated in the air, it yields metallic mercury and sulphurous oxide: it resists the action both of caustic alkalies in solution, and the strong mineral acids, even nitric, and is attacked only by nitromuriatic acid.

Mercurous sulphide, Hg_2S , is obtained by passing hydrogen sulphide into a solution of mercurous nitrate, as a black precipitate, which is resolved at a gentle heat into mercuric sulphide and metallic mercury.

Ammoniacal Mercury Compounds.—Mercurammonium Salts.

—By the action of ammonia and its salts on mercury compounds, a variety of substances are formed which may be regarded as salts of mercurammonium—that is, of ammonium-molecules in which the hydrogen is more or less replaced by mercury, in the proportion of 100 or 200 parts of mercury to 1 part of hydrogen, according as the compound is formed from a mercurous or a mercuric salt. The following are the most important of these compounds:—

Mercuric Compounds.—*Mercurio-diammonium chloride*, $(\text{N}_2\text{H}_5\text{Hg}'')\text{Cl}_2$, known in pharmacy as *fusible white precipitate*, is produced by adding potash to a solution of ammonio-mercuric chloride, $(2\text{NH}_4\text{Cl.HgCl}_2)$, or by dropping solution of mercuric chloride into a boiling solution of sal-ammoniac containing free ammonia, as long as the resulting precipitate redissolves: it then separates on cooling in regular dodecahedrons. At a gentle heat it gives off ammonia, leaving a chloride of mercurammonium and hydrogen, $(\text{NH}_2\text{Hg}')\text{Cl.HCl}$:



Mercurammonium chloride, $(\text{NH}_2\text{Hg}')\text{Cl}$.—This salt, known in pharmacy as *insoluble white precipitate*, is formed by adding ammonia to a solution of mercuric chloride. When first produced, it is bulky and white, but by contact with hot water, or by much washing with cold water, it is converted into hydrated dimercurammonium chloride, $\text{NHg}''\text{Cl.H}_2\text{O}$.

Trimercurio-diammonium nitrate, $(\text{N}_2\text{H}_5\text{Hg}''_3)(\text{NO}_3)_2.2\text{H}_2\text{O}$, is formed as a white precipitate, on mixing a dilute and very acid solution of mercurio nitrate with very dilute ammonia.

Trimercurio-diamine, $\text{N}_2\text{Hg}''_3$, a compound derived from a double molecule of ammonia, N_2H_6 , by substitution of 3 atoms of bivalent mercury for 6 atoms of hydrogen, is formed by passing dry ammonia gas over dry precipitated mercuric oxide:



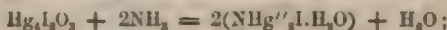
The excess of oxide being removed by nitric acid, the trimercuro-diamine is obtained as a dark brown powder, which explodes by heat, friction, percussion, or contact with oil of vitriol, almost as violently as nitrogen chloride.

Dimercurammonium chloride, $\text{NHg}''_2\text{Cl} \cdot \text{H}_2\text{O}$, is obtained, as already observed, by boiling mercuriodiammonium chloride (infusible white precipitate) with water. It is a heavy, granular, yellow powder, which turns white again when treated with sal-ammoniac.

Dimercurammonium iodide, $\text{NHg}''_2\text{I} \cdot \text{H}_2\text{O}$.—This compound may be formed by digesting the corresponding chloride in a solution of potassium iodide; or by heating mercuric iodide with excess of aqueous ammonia:



also by passing ammonia gas over mercuric oxy-iodide:



and, lastly, by adding ammonia to a solution of potassio-mercuric iodide mixed with caustic potash:

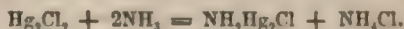


This last reaction affords an extremely delicate test for ammonia. A solution of potassio-mercuric iodide is prepared by adding potassium iodide to a solution of corrosive sublimate, till a portion only of the resulting red precipitate is redissolved, then filtering, and mixing the filtrate with caustic potash. The liquid thus obtained forms, with a very small quantity of ammonia, either free or in the form of an ammoniacal salt, a brown precipitate, soluble in excess of potassium iodide. This is called Nesler's test for ammonia.

Dimercurammonium Hydroxide, $\text{NHg}''_2(\text{HO})$.—This compound is formed by treating precipitated mercuric oxide with aqueous ammonia, or by treating either of the dimercurammonium salts with a caustic alkali. It is a brown powder, which dissolves in acids, yielding salts of dimercurammonium.

Dimercurammonium Sulphate, $(\text{NHg}''_2)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, formerly called *ammoniacal turpethum*, is prepared by dissolving mercuric sulphate in ammonia, and precipitating the solution with water. It is a heavy white powder, yellowish when dry, resolved by heat into water, nitrogen, ammonia, and mercurous sulphate.

Mercurous Compounds.—*Mercurousammonium Chloride*, $\text{NH}_2\text{Hg}'\text{Cl}$, is the black precipitate formed when dry calomel is exposed to the action of ammonia gas. When exposed to the air, it gives off ammonia and leaves white mercurous chloride.—*Dimercurousammonium chloride*, $\text{NH}_2\text{Hg}'_2\text{Cl}$, is formed, together with sal-ammoniac, by digesting calomel in aqueous ammonia:



It is gray when dry, and is not altered by boiling water.—*Dimercurousammonium nitrate*, $2(\text{NH}_2\text{Hg}'_2)\text{NO}_3 \cdot \text{H}_2\text{O}$. This, according to Kane, is the composition of the velvet-black precipitate known as Hahnemann's soluble mercury, which is produced on adding ammonia to a solution of mercurous nitrate. According to C. G. Mitscherlich, on the other hand, the precipitate thus formed has the composition $2\text{NH}_2\text{Hg}'_2\text{O} \cdot 3\text{Hg}_2\text{O}$, which is that of a hydrated trimercuroammonium nitrate, $2(\text{NHHg}'_2)\text{NO}_3 \cdot 2\text{H}_2\text{O}$.

Reactions of Mercury Salts.—All mercury compounds are volatilized or decomposed by a temperature of ignition: those which fail to yield the metal by simple heating may, in all cases, be made to do so by heating in a test-tube with a little dry sodium carbonate. The metal is precipitated from its soluble combinations by a plate of copper, and also by a solution of *caustic chloride* used in excess.

Hydrogen sulphide, and *Ammonium sulphide*, produce in solutions, both of mercuric and of mercurous salts, black precipitates insoluble in ammonium sulphide. In mercuric salts, however, if the quantity of the reagent added is not sufficient for complete decomposition, a white precipitate is formed, consisting of a compound of mercuric sulphide with the original salt, and often colored yellow or brown by excess of mercuric sulphide. An excess of hydrogen sulphide, or ammonium sulphide, instantly turns the precipitate black. This reaction is quite characteristic of mercuric salts.

Mercuric salts are further distinguished by forming a yellow precipitate with *caustic potash* or *soda*; white with *ammonia* or *ammonium carbonate*, insoluble in excess; red-brown with *potassium* or *sodium carbonate*. With *potassium iodide* they yield a bright scarlet precipitate, soluble in excess, either of the mercuric salt or of the alkaline iodide.

Mercurous salts are especially characterized by forming, with *ammonia* or *soluble chlorides*, a white precipitate which is turned black by ammonia. They also yield black precipitates with *caustic alkalis*; white with *alkaline carbonates*, soon turning black; greenish-yellow with *potassium iodide*.

Alloys of mercury with other metals are termed *amalgams*: mercury dissolves in this manner many of the metals, as gold, silver, tin, lead, etc. These combinations sometimes take place with considerable violence, as in the case of potassium, in which light and heat are produced; besides this, many of the amalgams after a while become solid and crystalline. The amalgams of tin used in silvering looking-glasses, and that of silver and of copper, sometimes employed for stopping hollow teeth, are examples. The solid amalgams appear to be, for the most part, definite compounds, while the liquid amalgams may be regarded, in many instances, as solutions of definite compounds in excess of mercury, inasmuch as, when they are pressed between chamois leather, mercury, containing only a small quantity of the other metal, passes through, while a solid amalgam, frequently of definite atomic constitution, remains behind. A native compound of mercury and silver, called "amalgam" by mineralogists, and having the composition Ag_2Hg_3 , or Ag_2Hg , is found crystallized in octohedrons, rhombic dodecahedrons, and other forms of the regular system.

CLASS III.—TRIAD METALS.

THALLIUM.

Atomic weight, 204. Symbol, Tl.

This element was discovered by Crookes, in 1861, in the seleniferous deposit of a lead-chamber of a sulphuric acid factory in the Hartz Mountains, where iron pyrites is used for the manufacture of sulphuric acid. The name is derived from *θαλλός*, "green," because the existence of this metal was first recognized by an intense green line, appearing in the spectrum of a flame in which thallium is volatilized. It was at first suspected to be a metalloid, but further examination proved it to be a true metal. It was first obtained in a distinct metallic form by Crookes towards the end of the year 1861, and soon afterwards by Lamy, who prepared it from the deposit in the lead-chamber of M. Kuhlmann, of Lille, where Belgian pyrites is employed for the manufacture of sulphuric acid.

Thallium appears to be very widely diffused as a constituent of iron and copper pyrites, though it never constitutes more than the 4000th part of the bulk of the ores. It has also been found in lepidolite from Moravia, in mica from Zinnwald in Bohemia, and in the mother-liquors of the salt works at Nauheim.

Thallium is most economically prepared from the flue-dust of pyrites burners. This substance is stirred up in wooden tubs with boiling water, and the clear liquor, siphoned off from the deposit, is mixed with excess of strong hydrochloric acid, which precipitates impure thallium monochloride. To obtain a pure salt, this crude chloride is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred, and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused acid sulphate is now to be dissolved in an excess of water, and an abundant stream of hydrogen sulphide passed through the solution. The precipitate, which may contain arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrogen sulphide is removed. The liquid is now to be rendered alkaline with ammonia, and boiled; the precipitate of iron oxide and alumina, which generally appears in this place, is filtered off; and the clear solution evaporated to a small bulk. Thallium sulphate then separates on cooling, in long, clear, prismatic crystals.

Metallic thallium may be reduced from the solution of the sulphate, either by electrolysis, or by the action of zinc.

Thallium is a heavy metal, resembling lead in its physical properties. When freshly cut, it exhibits a brilliant metallic lustre and grayish color, somewhat between those of silver and lead, assuming a slight yellowish tint by friction with harder bodies. It is very soft, being readily cut with a knife, and making a streak on paper like plumbago. It is very malleable, is not easily drawn into wire, but may be readily squeezed into that form by the process technically called "squirting." It has a highly crystalline structure, and crackles like tin when bent. It melts at 294°.

In contact with the air, thallium tarnishes more rapidly than lead, be-

being coated with a thin layer of oxide, which preserves the rest of the metal.

The most characteristic property of thallium is the bright green color which the metal or any of its compounds impart to a colorless flame; and this color, when viewed by the spectroscope, is seen to be absolutely monochromatic, appearing as one intensely brilliant and sharp green line.

Thallium dissolves in hydrochloric, sulphuric, and nitric acids, the latter attacking it very energetically, with copious evolution of red vapors.

Thallium forms two classes of compounds—namely, the thallious compounds, in which it is univalent; and the thallic compounds, in which it is trivalent. Thus it forms two oxides, Tl_2O and Tl_2O_3 , with corresponding chlorides, bromides, iodides, and oxygen-salts. In some of its chemical relations it resembles the alkali-metals, forming a readily soluble and highly alkaline monoxide, a soluble and alkaline carbonate, an insoluble platinumchloride, a thallic-aluminic sulphate, similar in form and composition to common potash-alum, and several phosphates exactly analogous in composition to the phosphates of sodium. In most respects, however, it is more nearly allied to the heavy metals, especially to lead, which it resembles closely in appearance, density, melting-point, specific heat, and electric conductivity.

Thallium Chlorides.—Thallium forms four chlorides, represented by the formulae $TlCl$, Tl_2Cl_2 , Tl_2Cl_4 , and $TlCl_3$; the second and third of which may be regarded as compounds of the monochloride and trichloride.

The *Monochloride* or *Thallious Chloride*, $TlCl$, is formed by direct combination, the metal burning when heated in chlorine gas; or as a white curdy precipitate, resembling silver chloride, by treating the solution of any thallious salt with a soluble chloride. When boiled with water it dissolves like lead chloride, and separates in white crystals on cooling. It forms double salts with trichloride of gold and tetrachloride of platinum. The *platinum salt*, $2TlCl.PtCl_6$, separates as a pale yellow very slightly soluble crystalline powder, on adding platinic chloride to thallious chloride.

The *Trichloride* or *Thallic chloride*, $TlCl_3$, is obtained by dissolving the trioxide in hydrochloric acid, or by acting upon thallium, or one of the lower chlorides, with a large excess of chlorine at a gentle heat. It is soluble in water, and separates by evaporation in a vacuum in hydrated crystals; melts easily, and decomposes at a high temperature. It forms crystalline double salts with the chlorides of the alkali-metals.

The *Sesquichloride*, $Tl_2Cl_3 = TlCl_2.3TlCl$, is produced by dissolving thallium or the monochloride in nitromuriatic acid, and separates on cooling in yellow crystalline scales. By aqueous ammonia, potash, or even by thallious oxide, it is instantly decomposed into sesquioxide and monochloride, according to the equation:



The *Dichloride*, $Tl_2Cl_4 = TlCl_2.TlCl$, is formed by carefully heating thallium or the monochloride, in a slow current of chlorine. It is a pale yellow substance reduced to sesquichloride by further heating.

The *Bromides* of thallium resemble the chlorides.

Iodides.—*Thallious Iodide*, THI , is formed by direct combination of its elements, or by double decomposition. It forms a beautiful yellow powder, rather darker than sulphur, and melting, below redness, to a scarlet liquid, which, as the mass cools, remains scarlet for some time after solidification, then changes to bright yellow. The dried precipitate, when spread on paper with a little gum-water, undergoes a similar but opposite change to

that experienced by mercuric iodide when heated, the yellow surface when held over a flame suddenly becoming scarlet, and frequently remaining so after cooling for several days; hard friction with a glass rod, however, changes the scarlet color back to yellow. It is very slightly soluble in water, requiring, according to Crookes, 4453 parts of water at 17.2°C , and 842.4 parts at 100° , to dissolve it.

Thallic Iodide, TI_3 , is formed by the action of thallium on iodine dissolved in ether, as a brown solution which gradually deposits rhombic prisms. It forms crystalline compounds with the iodides of the alkali-metals.

Thallium Oxides.—Thallium forms a monoxide and a trioxide.

The *Monoxide* or *Thallous Oxide*, TI_2O , constitutes the chief part of the crust which forms on the surface of the metal when exposed to the air. It may be prepared by allowing granulated thallium to oxidize in warm moist air, and then boiling with water. The filtered solution first deposits white needles of thallium carbonate, and, on further cooling, yellow needles of the hydroxide, TIHO or $\text{TI}_2\text{O} \cdot \text{H}_2\text{O}$, which, when left over oil of vitriol in a vacuum, yields the anhydrous monoxide as a reddish-black mass retaining the shape of the crystals. It is partially reduced to metal by hydrogen at a red heat. When fused with sulphur it yields thallious sulphide. It dissolves readily in water, forming a colorless strongly alkaline solution, which reacts with metallic salts very much like caustic potash. This solution treated with zinc, or subjected to electrolysis, yields metallic thallium.

The *Trioxide*, or *Thallic Oxide*, is the chief product obtained by burning thallium in oxygen gas. It is best prepared by adding potash to the solution of a thallic salt, and drying the precipitate at 260° . It is also formed by electrolysis of thallious sulphate. It is a dark red powder reduced to thallious oxide at a red heat; neutral, insoluble in water and in alkalis. Thallic hydrate, $\text{TI}''''\text{HO}$, is obtained by drying the above-mentioned precipitate at 100° .

Oxygen-salts.—Both the oxides of thallium dissolve readily in acids, forming crystalline salts, soluble in water; there are also a few insoluble thallium salts formed by double decomposition.

Thallious carbonate, TI_2CO_3 , is deposited in crystals, apparently trimetric, when a solution of thallious oxide is exposed to the air. It is soluble in water, and the solution has a slightly caustic taste and alkaline reaction.

Sulphates.—Thallious sulphate, TI_2SO_4 , obtained by evaporating the chloride or nitrate with sulphuric acid, or by heating metallic thallium with that acid, crystallizes in anhydrous rhombic prisms, isomorphous with potassium sulphate. It forms, with aluminium sulphate, the salt, $\text{AlTI}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, isomorphous with common alum; and with the sulphates of magnesium, nickel, etc., double salts containing 6 molecules of water, and isomorphous with magnesium and potassium sulphate, etc. (p. 256). *Thallic sulphate*, $\text{TI}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$, separates by evaporation from a solution of thallic oxide in dilute sulphuric acid, in thin colorless laminae, which are decomposed by water, even in the cold, with separation of brown thallic oxide.

Phosphates.—The thallious phosphates form a series nearly as complete as those of the alkali-metals, which they also resemble in their behavior when heated. There are three *orthophosphates*, containing respectively H_2TIPO_4 , HTI_2PO_4 , and TI_3PO_4 . The first two are soluble in water; the second is obtained by neutralizing dilute phosphoric acid at boiling heat with thallious carbonate, and the first by mixing the dithallious salt

with excess of phosphoric acid. The *trithallious salt*, Ti_3PO_4 , is very sparingly soluble, and is formed as a crystalline precipitate on mixing the saturated solutions of ordinary disodic phosphate and thallious sulphate; also, together with ammonio-thallious phosphate, by treating the monothallious or dithallious salt with excess of ammonia. There are two *thallous pyrophosphates*, $\text{H}_2\text{Ti}_2\text{P}_2\text{O}_7$, and $\text{Ti}_4\text{P}_2\text{O}_7$, both very soluble in water: the first produced by carefully heating monothallious orthophosphate, the second by strongly heating dithallious orthophosphate. Of *thallous metaphosphate*, TiPO_3 , there are two modifications: the first remaining as a slightly soluble vitreous mass when monothallious orthophosphate is strongly ignited, the second obtained as an easily soluble glass by igniting ammonio-thallious orthophosphate.

Thallic orthophosphate, $\text{Ti}^{\text{III}}\text{PO}_4 \cdot 2\text{H}_2\text{O}$, separates as an insoluble gelatinous precipitate on diluting a solution of thallic nitrate mixed with phosphoric acid.

Thallium Sulphide, Ti_2S .—This compound is precipitated from all thallous salts by ammonium sulphide, and from the acetate, carbonate, or oxalate, by hydrogen sulphide (incompletely also from the nitrate, sulphate, or chloride), in dense flocks of a grayish or brownish-black color. Thallic salts appear to be reduced to thallous salts by boiling with ammonium sulphide. Thallium sulphate projected into fused potassium cyanide is reduced to sulphide, which then forms a brittle metallic-looking mass, having the lustre of plumbago, and fusing more readily than metallic thallium.

Reactions of Thallium Salts.—The reactions of thallious salts with hydrogen sulphide and ammonium sulphide have just been mentioned. From their aqueous solutions thallium is rapidly precipitated in metallic crystals by zinc, slowly by iron. Soluble chlorides precipitate difficultly soluble white thallous chloride; soluble bromides throw down white, nearly insoluble bromide; soluble iodides precipitate insoluble yellow thallious iodide. Caustic alkalies and alkaline carbonates form no precipitate; sodium phosphate forms a white precipitate, insoluble in ammonia, easily soluble in acids.

Potassium chromate gives a yellow precipitate of thallious chromate insoluble in cold nitric or sulphuric acid, but turning orange-red on boiling in the acid solution. Platinic chloride precipitates a very pale-yellow insoluble double salt.

Thallic salts are easily distinguished from thallous salts by their behavior with alkalies, and with soluble chlorides or bromides. Their solutions give with ammonia, and with fixed alkalies and their carbonates, a brown gelatinous precipitate of thallic oxide, containing the whole of the thallium. Soluble chlorides or bromides produce no precipitate in solutions of pure thallic salts; but if a thallous salt is likewise present, a precipitate of sesquichloride or sesquibromide is formed. Oxalic acid forms in solutions of thallic salts a white pulverulent precipitate; phosphoric acid a white gelatinous precipitate; and arsenic acid a yellow gelatinous precipitate. Thallic nitrate gives with potassium ferrocyanide a green, and with the ferricyanide a yellow precipitate.

In examining a mixed metallic solution, thallium will be found in the precipitate thrown down by ammonium sulphide, together with iron, nickel, manganese, &c. From these metals it may be easily separated by precipitation with potassium iodide or platinic chloride, or by reduction to the metallic state with zinc.

Thallium salts are reduced before the blowpipe with charcoal and sodium

carbonate or potassium cyanide. The green color imparted to flame by thallium, and the peculiar character of its spectrum, have already been mentioned.

INDIUM.

Atomic weight, 113.4. Symbol, In.

This extremely rare metal was discovered in 1863 by Reich and Richter, in the zinc-blende of Freiberg, and has since been found in a few other zinc-ores and in the flue-dust of zinc furnaces. The metallic sponge, which remains when the crude zinc of the Freiberg works is dissolved in dilute sulphuric acid, contains the whole of the indium (0.045 per cent.), together with lead, arsenic, cadmium, and iron. It is dissolved in nitric acid; the lead, arsenic, and cadmium are precipitated by hydrogen sulphide; and the filtered solution is heated with potassium chlorate to bring all the iron to the state of ferric salt, and then treated with ammonia, which precipitates the indium as a hydroxide, together with iron and zinc. The precipitate is dissolved in acetic acid, the indium is precipitated as sulphide by hydrogen sulphide; and freed from traces of iron and zinc by dissolving the precipitate in dilute hydrochloric acid, precipitating the indium by agitation with barium carbonate, dissolving out the indium hydroxide by dilute sulphuric acid, and reprecipitating with ammonia.

Indium, reduced from its oxide by ignition with sodium, is a silver-white metal, soft and ductile, has a specific gravity of 7.421, melts at 170°C . (348.8°F .), and is less volatile than cadmium or zinc. When heated to redness in the air, it burns with a violet flame, and is converted into the yellow sesquioxide. Heated in chlorine, it burns with a yellow-green light, and forms a chloride, which sublimes without fusion at an incipient red heat in soft, white laminae.

Indium dissolves in the strong mineral acids, and is precipitated from the solutions by zinc and cadmium. Hydrogen sulphide precipitates it completely, as a yellow sulphide, from a solution of its acetate, and from neutral solutions of indium salts in general, but not from solutions containing excess of the strong mineral acids. Ammonia and sodium carbonate produce white precipitates insoluble in excess: caustic potash or soda throws down white indium hydroxide soluble in excess of the alkali. Ammonium carbonate forms a white precipitate soluble in excess, and reprecipitated on boiling. Barium carbonate precipitates indium completely.

The spectrum of indium is characterized by two indigo-colored lines, one very bright and more refrangible than the blue line of strontium, the other fainter and still more refrangible, and approaching the blue line of potassium. It was the observation of this peculiar spectrum that led to the discovery of the metal.

The formulae of the principal normal indium compounds are as follows:—

| | |
|--|--|
| Chloride | InCl_3 |
| Indium and ammonium chloride | $2\text{NH}_4\text{Cl}.\text{InCl}_3 + \text{H}_2\text{O}$ |
| Yellow oxide | In_2O_3 |
| Hydroxide | $\text{In}(\text{OH})_3$ |
| Nitrate | $\text{In}(\text{NO}_3)_3$ |
| Sulphate | $\text{In}_2(\text{SO}_4)_3 + 9\text{H}_2\text{O}$ |

The yellow oxide, heated in a stream of hydrogen, is successively reduced to a green, a gray, and a black oxide (In_2O_3), and at a low red heat to the metallic state.

GALLIUM.

Atomic weight, 69.6. Symbol, Ga.

This metal was discovered in 1875 by Lecoq de Boisbaudran,* in a zinc-blende from the mine of Pierrefitte, in the valley of Argeles, Pyrenees, and has likewise been found, though always in very small quantity, in blendes from other localities. It is separated by dissolving the blende in nitromuriatic acid, immersing plates of zinc in the solution till the disengagement of hydrogen becomes slow,—whereby copper, lead, cadmium, and other metals are precipitated,—and then boiling the clear liquid for several hours with a large excess of zinc, which throws down alumina, basic zinc-salts, and oxide of gallium. This precipitate is redissolved in hydrochloric acid, the solution again boiled with zinc; the resulting precipitate, which contains the gallium in a more concentrated form, is redissolved in hydrochloric acid; the solution mixed with ammonium acetate is treated with hydrogen sulphide, which throws down the zinc and gallium as sulphides, leaving the aluminium in solution; and this treatment is repeated to insure the complete separation of the alumina. The white sulphides of zinc and gallium are then dissolved in hydrochloric acid, the solution is fractionally precipitated with sodium carbonate, the gallium going down chiefly in the first portions; and, to complete the separation of the zinc, the gallium oxide is dissolved in sulphuric acid and reprecipitated by excess of ammonia; this dissolves all the zinc oxide, and the greater part of the gallium oxide, which may be reprecipitated by boiling the liquid to expel the free ammonia.

Metallic gallium is obtained by electrolyzing a solution of the oxide in potash or ammonia with platinum-electrodes, the gallium being deposited on the negative plate as a compact, closely adhering crust, which may be detached by bending the plate backwards and forwards under cold water.

Gallium is a hard metal somewhat whiter than platinum, and acquires a good polish by pressure; it is sectile and somewhat malleable; its specific gravity is 5.9, which is intermediate between that of aluminium (2.6) and that of indium (7.4). Its melting point is 30.1° C. (86.2° F.), so that it liquefies when pressed between the fingers; frequently also it remains liquid for a long time even when cooled to nearly 0°. The melted metal adheres to glass, forming a mirror whiter than that produced by mercury. When heated to bright redness in contact with the air, it oxidizes merely on the surface, and does not volatilize.

Gallium forms a very bright electric spectrum, exhibiting a brilliant line and a fainter band in the violet. In a gas-flame only the line is exhibited, and even this is very faint and fugitive. It was by these spectroscopic characters that the existence of gallium was first recognized.

Gallium chloride is very soluble and deliquescent. Its aqueous solution is clear when highly concentrated, but becomes turbid on addition of water; the precipitate (probably an oxychloride) dissolves but very slowly in hydrochloric acid. A slightly acidulated solution of the chloride evaporated at a gentle heat, deposits needles which act strongly on polarized light. The sulphate is not deliquescent.

Gallium forms an ammonia-alum, which crystallizes in octohedrons like common alum; it dissolves in cold water, but the solution becomes turbid on boiling, and is decomposed by heating with acetic acid. The existence

* Comptes Rendus, lxxxi. 403.

of this alum shows that the oxide of gallium is represented by the formula Ga_2O_3 , and its chloride by $GaCl_3$.

Solutions of gallium salts give with *ammonium sulphide* a white precipitate of gallium sulphide insoluble in excess of the reagent. The same precipitate is formed by *hydrogen sulphide* in presence of acetic, but not of hydrochloric acid. *Ammonia* and *carbonate of ammonia* give white precipitates soluble in excess. Slightly acid solutions of the chloride and sulphate are not precipitated in the cold by *ammonium acetate*; but the neutral solutions are clouded thereby. Gallium oxide is easily precipitated by *barium carbonate*.

In a mixed solution of gallium and aluminium, the latter is precipitated before the gallium, and in a mixed solution of gallium and indium, the gallium goes down first; in point of basicity, therefore, gallium is intermediate between aluminium and indium.

The atomic weight of gallium has not been determined by direct experiment; but as this metal is a triad intermediate in some of its properties (basicity and density) between aluminium and indium, and in its chemical reactions exhibits considerable resemblance to zinc, it is supposed to have an atomic weight not far from 68, as assigned to it in Mendeleeff's Classification of the Elements (p. 239).

CLASS IV.—TETRAD METALS.

TIN.

Atomic weight, 118. Symbol, Sn (Stannum).

Tin, a valuable metal, occurs in the state of oxide, and more rarely as sulphide: the principal tin mines are those of Saxony and Bohemia, Malaya, and more especially Cornwall. In Cornwall the tin-stone is found as a constituent of metal-bearing veins, associated with copper ore, in granite and slate-rocks; and as an alluvial deposit, mixed with rounded pebbles, in the beds of several small rivers. The first variety is called *ore*, and the second *stream-tin*. Tin oxide is also found disseminated through the rock itself in small crystals.

To prepare the ore for reduction, it is stamped to powder, washed, to separate as much as possible of the earthy matter, and roasted, to expel sulphur and arsenic: it is then strongly heated with coal, and the metal thus obtained is cast into large blocks. Two varieties of commercial tin are known, called *grain-* and *bar-tin*; the first is the best; it is prepared from the stream ore.

Pure tin has a white color, approaching that of silver: it is soft and malleable, and when bent or twisted emits a peculiar crackling sound; it has a density of 7.3, and melts at 237°C . (458.6°F .). Tin is but little acted upon by air and water, even conjointly; when heated above its melting-point, it oxidizes rapidly, becoming converted into a whitish powder, used in the arts for polishing, under the name of *putty powder*. The metal is attacked and dissolved by hydrochloric acid, with evolution of hydrogen; nitric acid acts with great energy, converting it into a white hydrate of the dioxide.

Tin is a tetrad metal, and forms two well-defined classes of compounds, namely, the stannous compounds, in which it is bivalent, as SnCl_2 , sulph. SnO , etc., and the stannic compounds, in which it is quadrivalent, as SnCl_4 , SnO_2 , etc.; also a few compounds called stannoso-stannic compounds, of intermediate composition, e. g., Sn_2Cl_3 , Sn_2O_3 , etc.

Chlorides.—The *dichloride*, or *Stannous Chloride*, SnCl_2 , is obtained in the anhydrous state by distilling a mixture of calomel and powdered tin, prepared by agitating the melted metal in a wooden box until it solidifies. It is a gray, resinous-looking substance, fusible below redness, and volatile at a high temperature.

The *hydrated chloride*, commonly called *tin salt*, is easily prepared by dissolving metallic tin in hot hydrochloric acid. It crystallizes in needles containing $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, which are freely soluble in a small quantity of water, but are apt to be decomposed in part when put into a large mass, unless hydrochloric acid in excess be present. Solution of stannous chloride is employed as a deoxidizing agent; it reduces the salts of mercury and other metals of the same class. It is also extensively employed as a mordant in dyeing and calico-printing; sometimes also as an antichlore.

Stannous chloride unites with the chlorides of the alkali-metals, forming crystallizable double salts, $\text{SnCl}_2 \cdot 2\text{KCl}$, etc., called *Stannosochlorides* or *Chlorostannites*.

The *tetrachloride*, or *Stannic chloride*, SnCl_4 , formerly called *fuming liquor of Linnæus*, is made by exposing metallic tin to the action of chlorine, or, more conveniently, by distilling a mixture of 1 part of powdered tin with 5 parts of corrosive sublimate. It is a thin, colorless, mobile liquid, boiling at 129°C , and yielding a colorless invisible vapor. It fumes in the air, and when mixed with a third part of water, solidifies to a soft fusible mass, called *butter of tin*. The solution of stannic chloride is much employed by the dyer for the brightening and fixing of red colors, and is sometimes designated by the old names, "composition, physis, or tin solution;" it is commonly prepared by dissolving metallic tin in a mixture of hydrochloric and nitric acids, care being taken to avoid too great elevation of temperature. The solution when evaporated yields a deliquescent crystalline hydrate $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

Stannic chloride forms, with the chlorides of the alkali-metals and alkaline earth-metals, crystalline double salts, called *stannochlorides* or *chlorostannates*, e. g., $\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$, $\text{SnCl}_4 \cdot \text{BaCl}_2$, etc. It also forms crystalline compounds with the pentachloride and oxychloride of phosphorus, viz., $\text{SnCl}_4 \cdot \text{PCl}_5$, and $\text{SnCl}_4 \cdot \text{POCl}_3$, and a solid compound with phosgene, containing $3\text{SnCl}_4 \cdot 2\text{PH}_2$.

The *trichloride*, or *Stannous chloride*, known only in solution, is produced by dissolving the sesquioxide in hydrochloric acid. The solution acts like a mixture of the dichloride and tetrachloride.

Fluorides.—*Stannous fluoride*, SnF_2 , obtained by evaporating the solution of stannous oxide in hydrofluoric acid, crystallizes in small shining opaque prisms. *Stannic fluoride*, SnF_4 , is not known in the free state, but unites with other metallic fluorides, forming crystalline compounds, called *stannofluorides* or *fluorostannates*, isomorphous with the corresponding aluminofluorides, titanofluorides, and zirconofluorides. The potassium salt contains $\text{SnF}_4 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$, the barium salt, $\text{SnF}_4 \cdot \text{BaF}_2$, etc.

Oxides.—The *monoxide* or *Stannous oxide*, SnO , is produced by heating stannous oxalate out of contact with the air; also by igniting stannous hydrate. This *hydrate*, $2\text{SnO} \cdot \text{H}_2\text{O}$, or $\text{Sn}_2\text{H}_2\text{O}_3$, is obtained as a white precipitate by decomposing stannous chloride with an alkaline carbonate, carbon dioxide gas being at the same time evolved. This hydrate, carefully washed, dried, and heated in an atmosphere of carbon dioxide, leaves anhydrous stannous oxide as a dense black powder, which is permanent in the air, but when touched with a red-hot body, takes fire and burns like tinder, producing the dioxide. The hydrate is freely soluble in caustic potash; the solution decomposes by keeping into metallic tin and dioxide. It dissolves also in sulphuric acid, forming *stannous sulphate*, SnSO_4 , which crystallizes in needles.

The *Sesquioxide*, Sn_2O_3 , is produced by the action of hydrated ferric oxide upon stannous chloride: it is a grayish, slimy substance, soluble in hydrochloric acid and in ammonia. This oxide has been but little examined.

The *dioxide*, or *Stannic oxide*, SnO_2 , occurs native as tin-stone or cassiterite, the common ore of tin, and is easily formed by heating tin, stannous oxide, or stannous hydrate in contact with the air. As thus prepared it is a white or yellowish amorphous powder, but by passing the vapor of stannic chloride mixed with aqueous vapor through a red-hot porcelain tube, it may be obtained in crystals. It is not attacked by acids even in the concentrated state.

Stannic oxide forms two hydrates, differing from one another in composition and proportion, both, however, being acids, and capable of forming salts by exchanging their hydrogen for metals. These hydrates or acids are *stannic acid*, $\text{SnO}_2 \cdot \text{H}_2\text{O}$, or H_2SnO_3 , and *metastannic acid*, Sn_2O_5 .

$2H_2O$, or $H_{10}Sn_3O_{15}$, the former being capable of exchanging the whole of its hydrogen for metal, and forming the stannates, containing M_2SnO_3 ; while the latter exchanges only one-fifth of its hydrogen, forming the metastannates, $H_2M_2Sn_3O_{15}$.

Stannic acid is precipitated by acids from solutions of alkaline stannates, also from solution of stannic chloride, by calcium or barium carbonate not in excess; alkaline carbonates throw down an acid stannate. When dried in the air at ordinary temperatures it has, according to Weber, the composition $SnO_2 \cdot 2H_2O$; in a vacuum half the water is given off, leaving $SnO_2 \cdot H_2O$.

Stannic hydrate dissolves in the stronger acids, forming the stannic salts, thus with sulphuric acid it forms *stannic sulphate*, $Sn(SO_4)_2$ or $SnO \cdot 2SO_3$. Hydrochloric acid converts it into the tetrachloride. The stannic salts of oxygen-acids are very unstable.

Stannates.—Stannic hydrate exhibits acid much more decidedly than basic properties. It forms easily soluble salts with the alkalis, and from these the insoluble stannates of the earth-metals and heavy metals may be obtained by precipitation. *Sodium stannate*, Na_2SnO_3 , which is much used in calico-printing as a "preparing salt" or mordant, is produced on the large scale by fusing tinstone with hydrate, nitrate, chloride, or sulphate of sodium; by boiling the tin ore with caustic soda-solution; by fusing metallic tin with a mixture of sodium nitrate and carbonate; or heating it with soda-solution mixed with sodium nitrate and chloride.*

Metastannic acid is produced by the action of nitric acid upon tin. When dried in the air at ordinary temperatures it contains $5SnO_2 \cdot 10H_2O$ or $H_2Sn_5O_{15} \cdot 5H_2O$, but at 100° it gives off 5 molecules of water, and is reduced to $H_2Sn_5O_{15}$. It is a white crystalline powder insoluble in water and in acids. It dissolves slowly in alkalis, forming metastannates, but it is gradually deposited in its original state as the solution absorbs carbonic

acid from the air. The *potassium salt*, $K_2H_2Sn_3O_{15}$ or $\frac{K_2O}{4H_2O} \cdot (SnO_2)_3$, may be precipitated in the solid state by adding pieces of solid potash to a solution of metastannic acid in cold potash. It is gummy, uncrystallizable, and strongly alkaline. The *sodium salt*, $Na_2H_2Sn_3O_{15}$, prepared in like manner, is crystallo-granular, and dissolves slowly, but completely, in water. The metastannates exist only in the hydrated state, being decomposed when deprived of their basic water.

Tin Sulphides.—The *monosulphide*, SnS , is prepared by fusing tin with excess of sulphur, and strongly heating the product. It is a lead-gray, brittle substance, fusible at a red heat, and soluble, with evolution of sulphuretted hydrogen, in hot hydrochloric acid. A *sesquisulphide* may be formed by gently heating the above compound with a third of its weight of sulphur: it is yellowish-gray, and easily decomposed by heat. The *disulphide*, SnS_2 , or *Mosaic gold*, is prepared by exposing to a low red heat, in a glass flask, a mixture of 12 parts of tin, 6 of mercury, 6 of sal-ammoniac, and 7 of flowers of sulphur. Sal-ammoniac, cinnabar, and stannous chloride sublime, while the bisulphide remains at the bottom of the vessel in the form of brilliant gold-colored scales: it is used as a substitute for gold powder. The same compound is obtained as an amorphous light-yellow powder by passing hydrogen sulphide into a solution of stannic chloride.

* Richardson and Watts's Chemical Technology, vol. I. part IV. p. 35, and part V. p. 342.

Stannous salts give with:—

Fixed caustic alkalis: white hydrate, soluble in excess.

Ammonia: carbonates of potassium, sodium and ammonium } white hydrate, nearly insoluble in excess.

Hydrogen sulphide . . } black-brown precipitate of monosulphide
Ammoniumsulphide . . } soluble in ammonium sulphide containing
 excess of sulphur, and reprecipitated by
 acids as yellow bisulphide.

Stannic salts give with:—

Fixed caustic alkalis: white hydrate, soluble in excess.

Ammonia: white hydrate, slightly soluble in excess.

Alkaline carbonates: white hydrate, slightly soluble in excess.

Ammonium carbonate: white hydrate, insoluble.

Hydrogen sulphide: yellow precipitate of bisulphide.

Ammonium sulphide: the same, soluble in excess.

Trichloride of gold, added to a dilute solution of stannous chloride, gives rise to a brownish-purple precipitate, called *purple of Cassius* (page 325).

The useful applications of tin are very numerous. *Tinned plate* consists of iron superficially alloyed with this metal, *namely*, of the best kind, chiefly tin, hardened by the admixture of a little antimony, etc. Cooking-vessels of copper are usually tinned in the interior. The use of tin solutions in dyeing and calico-printing has been already mentioned.

TITANIUM.

Atomic weight, 60. Symbol, Ti.

This is one of the rarer metals, and is never found in the metallic state. The most important titanium minerals are *rutile*, *brookite*, and *anatase*, which are different forms of titanic oxide, and the several varieties of titaniferous iron, consisting of ferrous titanate, sometimes alone, but more generally mixed with ferric or ferrous-ferric oxide. Occasionally, in the slag adhering to the bottom of blast-furnaces in which iron ore is reduced, small brilliant copper-colored cubes, hard enough to scratch glass, and in the highest degree infusible, are found. This substance, of which a single smelting furnace in the Hartz produced as much as 80 pounds, was formerly believed to be metallic titanium. Wöhler, however, has shown it to be a combination of titanium cyanide with titanium nitride. When the crystals are powdered, mixed with potassium hydrate, and fused, ammonia is evolved, and potassium titanate is formed. Metallic titanium in a finely divided state may be obtained by heating titanium and potassium fluoride with potassium. This element is remarkable for its affinity for nitrogen when heated in the air, it simultaneously absorbs oxygen and nitrogen.

Titanium is tetradic, like tin, and forms two classes of compounds: the titanic compounds, in which it is quadrivalent, *e. g.*, $TiCl_4$, TiO_2 , are the titanous compounds, in which it is apparently trivalent, but really

also quadrivalent, *e. g.*, Ti_2Cl_6 , or $TiCl_3$.

Chlorides.—*Titanous chloride*, $TiCl_3$, is produced by passing the vapor of titanous chloride mixed with hydrogen through a red-hot tube; it forms dark violet scales having a strong lustre. *Titanic chloride*, $TiCl_4$, is prepared by passing chlorine over an ignited mixture of titanous oxide and charcoal. It is a colorless, volatile, fuming liquid, having a specific gravity of 1.7609 at 0° C. (32° F.), vapor-density = 6.658, and boiling at 136° C. (275° F.). It unites very violently with water, and forms definite compounds with ammonia, ammonium chloride, hydrogen cyanide, cyanogen chloride, phosphine, and sulphur tetrachloride.

Fluorides.—*Titanous fluoride*, TiF_3 , is obtained as a violet powder by treating potassio-titanous fluoride in hydrogen gas, and treating the resulting mass with hot water. *Titanic fluoride*, TiF_4 , passes over as a fuming colorless liquid, when titanous oxide is distilled with fluor-spar and fuming sulphuric acid in a platinum apparatus. It unites with hydrofluoric acid and metallic fluorides, forming double salts called titanofluorides, or fluorotitanates, isomorphous with the silicofluorides, zirconfluorides, &c., $TiF_4 \cdot 2KF$; $TiF_4 \cdot CaF_2$.

Oxides.—The sesquioxide, or *Titanous oxide*, Ti_2O_3 , is obtained by igniting the dioxide in hydrogen, as a black powder, which, when heated in the air to a very high temperature, oxidizes to titanous oxide.

The dioxide, or *Titanic oxide*, occurs native in three different forms, viz., brookite and anatase, which are dimetric, and brookite, which is trimetric; of these, anatase is the purest, and rutile the most abundant. To obtain pure titanous oxide, rutile or titaniferous iron ore, reduced to fine powder, is fused with twice its weight of potassium carbonate, and the fused mass is dissolved in dilute hydrofluoric acid, whereupon titanous fluoride of potassium soon begins to separate. From the hot aqueous solution of this salt, ammonia throws down snow-white ammonium titanate, which is easily soluble in hydrochloric acid, and when ignited gives reddish-brown lumps of titanous oxide. This oxide is insoluble in water, and in all acids except strong sulphuric acid. By fusing it with six times its weight of potassium sulphate, a clear yellow mass is obtained, which dissolves perfectly in warm water.

Titanous oxide appears to form two hydrates or acids, analogous to stannous and metastannous acids. One of these, called titanous acid, is precipitated by ammonia from a solution of titanous chloride, as a white powder, which dissolves easily in sulphuric, nitric, and hydrochloric acids, even when these acids are rather dilute; but these dilute solutions, when boiled, deposit metatitanous hydrate as a soft, white powder, which, like the anhydrous oxide, is insoluble in all acids except strong sulphuric acid.

The titanates have not been much studied; most of them may be represented by the formulæ $M, TiO_3 = 2M_2O \cdot TiO_3$, and $M, TiO_3 = M_2O \cdot TiO_3$, (the symbol M denoting a univalent metal). The titanates of calcium and iron occur as natural minerals. The titanates of the alkali-metals are formed by fusing titanous oxide with alkaline hydrates, carbonates, or sulphates—some of them also in the wet way. When finely pulverized and levigated, they dissolve in moderately warm, concentrated hydrochloric acid; but the greater part of the dissolved titanous acid is precipitated on boiling the solution with dilute acids. The neutral titanates of the alkali-metals, M, TiO_3 , are insoluble in water, but soluble in acids. The titanates of the earth-metals and heavy metals are insoluble, and may be obtained by precipitation.

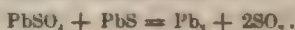
In a solution of titanous acid in hydrochloric acid, containing as little free acid as possible, *tincture of galls* produces an orange-colored precipi-

tate; *potassium ferrocyanide*, a dark-brown precipitate. Titanic oxide fused with *borax*, or, better, with *microcosmic salt*, in the inner blowpipe flame, forms a glass which is yellow while hot, but becomes violet on cooling. The delicacy of the reaction is much increased by melting a little metallic zinc in the bead.

LEAD.

Atomic weight, 207. Symbol, Pb (Plumbum).

This abundant and useful metal is altogether obtained from the native sulphide, or *galena*, no other lead-ore being found in large quantity. The reduction is effected in a reverberatory furnace, into which the crushed lead-ore is introduced and roasted for some time at a dull red heat, by which much of the sulphide becomes changed by oxidation to sulphate. The contents of the furnace are then thoroughly mixed, and the temperature raised, when the sulphate and sulphide react upon each other, producing sulphurous oxide and metallic lead:—



Lead is a soft bluish metal, possessing very little elasticity; its specific gravity is 11.45. It may be easily rolled out into plates, or drawn out into coarse wires, but has very little tenacity. It melts at 315.5°C . (599.4°F.), or a little above, and boils and volatilizes at a white heat. By slow cooling, it may be obtained in octohedral crystals. In moist air this metal becomes coated with a film of gray matter, thought to be suboxide, and when exposed to the atmosphere in the melted state it rapidly absorbs oxygen. Dilute acids, with the exception of nitric acid, act but slowly upon lead.

Lead is a tetrad, as shown by the constitution of plumbic ethide, $\text{Pb}(\text{C}_2\text{H}_5)_4$; but in its inorganic combinations it appears dyadic, forming but one chloride, PbCl_2 , with corresponding bromide and iodide. The oxide corresponding with these is PbO , and there are also higher oxides in which the metal may be regarded either as a dyad or as a tetrad: thus

the dioxide PbO_2 may be formulated either as $\text{O}=\text{Pb}=\text{O}$, or as $\text{Pb} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$.

Lead Chloride, PbCl_2 , is prepared by precipitating a solution of lead nitrate or acetate with hydrochloric acid or common salt. It separates as a heavy white crystalline precipitate, which dissolves in about 33 parts of boiling water, and separates again, on cooling, in needle-shaped crystals.

There are several oxychlorides of lead, one of which, $\text{Pb}_2\text{Cl}_2\text{O}_3$, or $\text{PbCl}_2 \cdot 2\text{PbO}$, occurs crystallized in right rhombic prisms on the Mendip Hills, thence called *mendipite*. Another, constituting Pattinson's white oxychloride, $\text{Pb}_2\text{Cl}_2\text{O}$ or $\text{PbCl}_2 \cdot \text{PbO}$, is prepared for use as a pigment by grinding galena with strong hydrochloric acid, dissolving the resulting chloride in hot water, and precipitating with lime-water. A third oxychloride, $\text{PbCl}_2 \cdot 7\text{PbO}$, called *patent yellow* or *Turner's yellow*, is prepared by heating 1 part of sal-ammoniac with 10 parts of litharge.

Lead Iodide, PbI_2 , is precipitated, on mixing lead nitrate or acetate with potassium iodide, as a bright yellow powder, which dissolves in

boiling water, and crystallizes therefrom in beautiful yellow iridescent scales.

Oxides.—The monoxide, PbO , called *litharge* or *massicot*, is the product of the direct oxidation of the metal. It is most conveniently prepared by heating the carbonate to dull redness; common *litharge* is impure monoxide which has undergone fusion. Lead oxide has a delicate straw-yellow color, is very heavy, and slightly soluble in water, giving an alkaline liquid. It is soluble in potash, and crystallizes from the solution in rhombic prisms. At a red heat it melts, and tends to crystallize on cooling. In the melted state it attacks and dissolves silicious matter with astonishing facility, often penetrating an earthen crucible in a few minutes. It is easily reduced when heated with organic substances of any kind containing carbon or hydrogen. It forms a large class of salts, often called *plumbic salts*, which are colorless if the acid itself is not colored.

Triplumbic tetroxide, or *Red lead*, is not of very constant composition, but generally contains Pb_3O_4 or $2PbO.PbO_2$. It is prepared by exposing the monoxide, which has not been fused, for a long time to the air, at a very faint red heat; it is a brilliant red and extremely heavy powder, decomposed, with evolution of oxygen, by a strong heat, and converted by acids into a mixture of monoxide and dioxide. It is used as a cheap substitute for vermilion.

The dioxide, PbO_2 , often called *puce* or *bruen lead-oxide*, is obtained without difficulty by digesting red lead in dilute nitric acid, whereby lead nitrate is dissolved out, and insoluble dioxide left behind in the form of a deep-brown powder. The dioxide is decomposed by a red heat, yielding up one-half of its oxygen. Hydrochloric acid converts it into lead chloride, with disengagement of chlorine; hot oil of vitriol forms with it lead sulphate, and liberates oxygen. The dioxide is very useful in separating sulphurous acid from certain gaseous mixtures, lead sulphate being then produced: $PbO_2 + SO_2 = PbSO_4$.

Triplumbic oxide, or *Lead suboxide*, Pb_3O , is formed when the monoxide is heated to dull redness in a retort: a gray pulverulent substance is then left, which is resolved by acids into monoxide and metal. It absorbs oxygen with great rapidity when heated, and even when simply moistened with water and exposed to the air.

Lead Nitrate, $Pb(NO_3)_2$, or $PbO.N_2O_5$, may be obtained by dissolving lead carbonate in nitric acid, or by acting directly upon the metal by the same agent with the aid of heat: it is, as already noticed, a by-product in the preparation of the dioxide. It crystallizes in anhydrous octohedrons, which are usually milk-white and opaque. It dissolves in $7\frac{1}{2}$ parts of cold water, and is decomposed by heat, yielding nitrogen tetroxide, oxygen, and lead monoxide, which obstinately retains traces of nitrogen. When a solution of this salt is boiled with an additional quantity of lead, and a portion of the latter is dissolved, and a basic nitrate generated, which may be obtained in crystals. Carbonic acid separates this excess of oxide in the form of a white compound of carbonate and hydrate of lead.

Neutral and basic compounds of lead oxide with the trioxide and tetroxide of nitrogen, have been described. These last are probably formed by the combination of a nitrite with a nitrate.

Lead Carbonate; White Lead; $PbCO_3$ or $PbO.CO_2$.—This salt is sometimes found beautifully crystallized in long white needles, accompanying other metallic ores. It may be prepared artificially by precipitating in the cold a solution of the nitrate or acetate with an alkaline carbonate: when the lead solution is boiling, the precipitate is a basic salt containing

$2\text{PbCO}_3, \text{PbH}_2\text{O}_3$. It is also manufactured to an immense extent by other means for the use of the painter. Pure lead carbonate is a soft white powder, of great specific gravity, insoluble in water, but easily dissolved by dilute nitric or acetic acid. Of the many methods put in practice, or proposed, for making white lead, the two following are the most important and interesting. One of these consists in forming a basic nitrate or acetate of lead by boiling finely powdered litharge with the neutral salt. This solution is then brought into contact with carbonic acid gas, whereby all the excess of oxide previously taken up by the neutral salt is at once precipitated as white lead. The solution strained or pressed from the latter is again boiled with litharge, and treated with carbonic acid: these processes are susceptible of indefinite repetition, whereby the little loss of neutral salt left in the precipitates is compensated. The second, and by far the more ancient method, is rather more complex, and at first sight not very intelligible. A great number of earthen jars are prepared, into each of which is poured a few ounces of crude vinegar; a roll of sheet lead is then introduced in such a manner that it shall neither touch the vinegar nor project above the top of the jar. The vessels are next arranged in a large building, side by side, upon a layer of stable manure, or, still better, spent tan, and closely covered with boards. A second layer of tan is spread upon the top of the latter, and then a second series of pots; these are in turn covered with boards and decomposing bark, and in this manner a pile of many alternations is constructed. After the lapse of a considerable time, the pile is taken down and the sheets of lead are removed and carefully unrolled; they are then found to be in great part converted into carbonate, which merely requires washing and grinding to be fit for use. The nature of this curious process is generally explained by supposing the vapor of vinegar raised by the high temperature of the fermenting matter, merely to act as a carrier between the carbonic acid evolved from the tan and the lead oxide formed under the influence of the acid vapor, a neutral acetate, a basic acetate, and a carbonate being produced in succession, and the action gradually travelling from the surface inwards. The quantity of acetic acid used is, in relation to the lead, quite trifling, and cannot directly contribute to the production of the carbonate. A preference is still given to the product of this old mode of manufacture, on account of its superior opacity, or *body*, over that obtained by precipitation. Commercial white lead, however prepared, always contains a certain proportion of hydrate. It is sometimes adulterated with barium sulphate.

When clean metallic lead is put into pure water and exposed to the air, a white, crystalline, scaly powder begins to show itself in a few hours, and very rapidly increases in quantity. This substance may consist of lead hydrate, formed by the action of the oxygen dissolved in the water upon the lead. It is slightly soluble, and may be readily detected in the water. In most cases, however, the formation of this deposit is due to the action of the carbonic acid dissolved in the water: it consists of carbonate in combination with hydrate, and is nearly insoluble in water. When common river or spring water is substituted for the pure liquid, this effect is less observable, the little sulphate, almost invariably present, causing the deposition of a very thin but closely adherent film of lead sulphate upon the surface of the metal, which protects it from further action. It is on this account that leaden cisterns are used with impunity, at least in most cases, for holding water: if the latter were quite pure, it would be speedily contaminated with lead, and the cistern would be soon destroyed. Natural water highly charged with carbonic acid cannot, under any circumstances, be kept in lead or passed through leaden pipes with safety, the carbonate, though insoluble in pure water, being slightly soluble in water containing carbonic acid.

The soluble salts of lead behave with reagents as follows :—

Caustic potash and soda precipitate a white hydrate freely soluble in excess. *Ammonia* gives a similar white precipitate, not soluble in excess. *The carbonates of potassium, sodium, and ammonium* precipitate lead carbonate, insoluble in excess. *Sulphuric acid or a sulphate* causes a white precipitate of lead sulphate, insoluble in nitric acid. *Hydrogen sulphide and ammonium sulphide* throw down black lead sulphide. *Lead* is readily detected before the blow-pipe by fusing the compound under examination on charcoal with sodium carbonate, when a bead of metal is easily obtained, which is recognized by its chemical as well as physical properties.

An alloy of 2 parts of lead and 1 of tin constitutes *plumber's solder*; these proportions reversed give a more fusible compound, called *fine solder*. The lead employed in the manufacture of shot is combined with a little arsenic.

CLASS V.—PENTAD METALS.

ANTIMONY.

Atomic weight, 122. Symbol, Sb (Stibium).

This important metal is found chiefly in the state of sulphide. It is freed by fusion from earthy impurities, and is afterwards decomposed by heating with metallic iron or potassium carbonate, which retains the sulphur.

Antimony has a bluish-white color and strong lustre: it is extremely brittle, being reduced to powder with the utmost ease. Its specific gravity is 6.8; it melts at a temperature just short of redness, and boils and volatilizes at a white heat. It has always a distinct, crystalline, platy structure, but by particular management it may be obtained in crystals, which are rhombohedral.* It is not oxidized by the air at common temperature; when strongly heated, it burns with a white flame, producing oxide, which is often deposited in beautiful crystals. It is dissolved by hot hydrochloric acid, with evolution of hydrogen and production of chloride. Nitric acid oxidizes it to antimonious acid, which is insoluble in that liquid.

Antimony forms two classes of compounds, the antimonious compounds in which it is trivalent, as SbCl_3 , Sb_2O_3 , Sb_2S_3 , etc., and the antimonious compounds in which it is quinquevalent, as SbCl_5 , Sb_2O_5 , Sb_2S_5 , etc.

Chlorides.—The trichloride or *Antimonious chloride*, SbCl_3 , formerly called *butter of antimony*, is produced when hydrogen sulphide is prepared by the action of strong hydrochloric acid on antimonious sulphide. The impure and highly acid solution thus obtained is put into a retort and distilled until each drop of the condensed product, on falling into the aqueous liquid of the receiver, produces a copious white precipitate. The receiver is then changed and the distillation continued. Pure antimonious chloride then passes over, and solidifies on cooling to a white, highly crystalline mass, from which the air must be carefully excluded. The same compound is formed by distilling metallic antimony in powder with $2\frac{1}{2}$ times its weight of corrosive sublimate. Antimonious chloride is very deliquescent: it dissolves in strong hydrochloric acid without decomposition, and the solution poured into water gives rise to a white bulky precipitate which, after a short time, becomes highly crystalline, and assumes a yellow fawn color. This is the old *powder of Algaroth*; it is a compound of chloride and trioxide of antimony. Alkaline solutions extract the chloride and leave the oxide. Finely powdered antimony thrown into chlorine gas takes fire.

The pentachloride or *Antimonic chloride*, SbCl_5 , is formed by passing a stream of chlorine gas over gently heated metallic antimony: a mixture of the two chlorides results, which may be separated by distillation. The pentachloride is a colorless volatile liquid, which forms a crystalline compound with a small portion of water, but is decomposed by a larger quantity into antimonious and hydrochloric acids.

* On electrolyzing a solution of one part of tartar-emetic in 4 parts of antimonious chloride by a small battery of two elements, antimony forming the positive and metallic copper of the negative pole, crusts of antimony are obtained, which possess the remarkable property of exploding and catching fire when cracked or broken.—Gore, *Proceedings of the Royal Society*, ix. 70.

Antimonious Hydride. Antimonetted Hydrogen. Stibine, SbH_3 .—When zinc is put into a solution of antimonious oxide, and sulphuric acid added, part of the hydrogen combines with the antimony, and the resulting gas, which is a mixture of stibine with free hydrogen, burns with a greenish flame, giving rise to white fumes of antimonious oxide. When the gas is conducted through a red-hot glass tube of narrow dimensions, or burned with a limited supply of air, as when a cold porcelain surface is pressed into the flame, metallic antimony is deposited. On passing a current of antimonetted hydrogen through a solution of silver nitrate, a black precipitate is obtained, containing SbAg_3 : from the formation of this compound it is inferred that the gas has the composition SbH_3 , analogous to ammonia, phosphine, and arsine. There are also several analogous compounds of antimony with alcohol-radicles, such as trimethylstibine, $\text{Sb}(\text{C}_2\text{H}_5)_3$, triethylstibine, $\text{Sb}(\text{C}_2\text{H}_5)_3$, etc.

Oxides.—Antimony forms two oxides, Sb_2O_3 and Sb_2O_5 , analogous to the chlorides, the first being a basic and the second an acid oxide, also an intermediate neutral oxide, Sb_2O_4 . The trioxide, or *Antimonious oxide*, Sb_2O_3 , occurs native, though rarely, as *valentinite*, or *white antimony*, in shining white trimetric crystals; also as *senarmontite* in regular octohedrons: it is therefore dimorphous. It may be prepared by several methods: as by burning metallic antimony at the bottom of a large red-hot crucible, in which case it is obtained in brilliant crystals; or by pouring solution of antimonious chloride into water, and digesting the resulting precipitate with a solution of sodium carbonate. The oxide thus produced is anhydrous; it is a pale buff-colored powder, fusible at a red heat, and volatile in a closed vessel, but in contact with air at a high temperature, it absorbs oxygen and becomes changed into the tetroxide. When boiled with cream of tartar (acid potassium tartrate), it is dissolved, and the solution yields on evaporation crystals of *tartar emetic*, which is almost the only antimonious salt that can bear admixture with water without decomposition. An impure oxide for this purpose is sometimes prepared by carefully roasting the powdered sulphide in a reverberatory furnace, and raising the heat at the end of the process, so as to fuse the product: it has long been known under the name *glass of antimony*, or *vitrum antimonii*.

Antimonious oxide likewise acts as a feeble acid, forming salts called *antimonates* which, however, are very unstable.

The tetroxide, or *Antimonous-antimonic oxide*, Sb_2O_4 , or $\text{Sb}_2\text{O}_3 \cdot \text{Sb}_2\text{O}_5$, occurs native as *cerantite*, or *antimony ochre*, in acicular crystals, or as a crust or powder. It is the ultimate product of the oxidation of the metal by heat and air: it is a grayish-white powder, infusible and non-volatile, insoluble in water and acids, except when recently precipitated. On treating it with tartaric acid (acid potassium tartrate), antimonious oxide is dissolved, antimonic acid remaining behind; and when a solution of the tetroxide in hydrochloric acid is gradually dropped into a large quantity of water, antimonious oxide is precipitated, while antimonic acid remains dissolved. From these and similar reactions, it has been inferred that the tetroxide is a compound of trioxide and pentoxide. On the other hand, it is sometimes regarded as a distinct oxide, because it dissolves without decomposition in alkalis, forming salts (often called *antimonites*), which may be obtained in the solid state. Two potassium salts, for example, have been formed, containing $\text{K}_2\text{O} \cdot \text{Sb}_2\text{O}_4$ and $\text{K}_2\text{O} \cdot 2\text{Sb}_2\text{O}_4$; and a calcium salt, $3\text{CaO} \cdot 2\text{Sb}_2\text{O}_4$, occurs as a natural mineral, called *romeine*. These salts may, however, be regarded as compounds of antimonates and antimonicites (containing Sb_2O_5): thus, $2(\text{K}_2\text{O} \cdot \text{Sb}_2\text{O}_4) = \text{K}_2\text{O} \cdot \text{Sb}_2\text{O}_3 + \text{K}_2\text{O} \cdot \text{Sb}_2\text{O}_5$.

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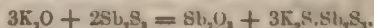
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The pentoxide, or *Antimonic oxide*, Sb_2O_5 , is formed as an insoluble hydrate when strong nitric acid is made to act upon metallic antimony, and,

on exposing this hydrate to a heat short of redness, it yields the anhydrous pentoxide as a pale straw-colored powder, insoluble in water and acids. It is decomposed by a red heat, yielding the tetroxide.

Hydrated antimonious oxide is likewise obtained by decomposing antimony pentachloride with an excess of water, hydrochloric acid being formed at the same time. The hydrated oxides, or acids, produced by the two processes mentioned, differ in many of their properties, and especially in their deportment with bases. The acid produced by nitric acid, called antimonious acid, is monobasic, producing normal salts of the form $M_2O \cdot Sb_2O_5$, or $MSbO_3$, and acid salts containing $M_2O \cdot 2Sb_2O_5$, or $2MSbO_3 \cdot Sb_2O_5$. The other, called metantimonious acid, is bibasic, forming normal salts containing $2M_2O \cdot Sb_2O_5$, or $M_4Sb_2O_9$, and acid salts containing $2M_2O \cdot 2Sb_2O_5$, or $M_4O \cdot Sb_2O_9$, so that the acid metantimonates are isomeric or polymeric with the normal antimonates. Among the metantimonates an acid potassium salt, $K_2O \cdot Sb_2O_5 \cdot 7H_2O$, is to be particularly noticed as yielding a precipitate with sodium salts: it is, indeed, the only reagent which precipitates sodium. It is obtained by fusing antimonious oxide with an excess of potash in a silver crucible, dissolving the fused mass in a small quantity of cold water, and allowing it to crystallize in a vacuum. The crystals consist of normal potassium metantimonate, $2K_2O \cdot Sb_2O_5$, and, when dissolved in pure water, are decomposed into free potash and acid metantimonate.

Sulphides.—The trisulphide, or *Antimonious sulphide*, Sb_2S_3 , occurs native as a lead-gray, brittle substance, having a radiated crystalline texture, and easily fusible. It may be prepared artificially by melting together antimony and sulphur. When a solution of tartar-emetic is precipitated by hydrogen sulphide, a brick-red precipitate falls, which is the same substance combined with a little water. If the precipitate be dried and gently heated, the water may be expelled without other change of color than a little darkening, but at a higher temperature it assumes the color and aspect of the native sulphide. This remarkable change probably indicates a passage from the amorphous to the crystalline state. When powdered antimonious sulphide is boiled in a solution of caustic potash, it is dissolved, antimonious oxide and potassium sulphide being produced; and the latter unites with an additional quantity of antimonious sulphide to form a soluble sulphur salt, in which the potassium sulphide is the sulphur-base, and the antimonious sulphide is the sulphur-acid:



The antimonious oxide separates in small crystals from the boiling solution when the latter is concentrated, and the sulphur-salt dissolves an extra portion of antimonious sulphide, which it again deposits on cooling as a red amorphous powder, containing a small admixture of antimonious oxide and potassium sulphide. This is the *kermes mineral* of the old chemists. The filtered solution mixed with an acid gives a potassium salt, hydrogen sulphide, and precipitated antimonious sulphide. Kermes may also be made by fusing a mixture of 5 parts antimonious sulphide and 3 of dry sodium carbonate, boiling the mass in 80 parts of water, and filtering while hot: the compound separates on cooling. The compounds of antimonious sulphide, with basic sulphides are called *sulphantimonites*; many of them occur as natural minerals. For example: zinkenite, $PbS \cdot Sb_2S_3$; feather-ore, $2PbS \cdot Sb_2S_3$; boulangerite, $3PbS \cdot Sb_2S_3$; faldore, or tetrahedrite, $4Cu_2S \cdot Sb_2S_3$, the antimony being more or less replaced by arsenic, and the copper by silver, iron, zinc, and mercury.

The *pentasulphide*, or *Antimonic sulphide*, Sb_2S_5 , formerly called *sulphur auratum*, is also a sulphur-acid, forming salts called *sulphantimonates*, most of which have the composition $3M_2S \cdot Sb_2S_5$ or M_3SbS_4 , analogous to the

normal orthophosphates and arsenates. When 18 parts of finely powdered antimonious sulphide, 17 parts dry sodium carbonate, 13 parts slaked lime, and $3\frac{1}{2}$ parts sulphur, are boiled in water for some hours, calcium carbonate, sodium antimonate, antimony pentasulphide, and sodium sulphide are produced. The first is insoluble, and the second partially so: the two last-named bodies, on the contrary, unite to form soluble sodium sulphantimonate, Na_3SbS_4 , which may be obtained by evaporation in beautiful crystals. A solution of this substance, mixed with dilute sulphuric acid, furnishes sodium sulphate, hydrogen sulphide, and antimony pentasulphide, which falls as a golden-yellow flocculent precipitate.

The sulphantimonates of the alkali-metals and alkaline earth metals are very soluble in water, and crystallize for the most part with several molecules of water. Those of the heavy metals are insoluble, and are obtained by precipitation.

The few salts of antimony soluble in water are distinctly characterized by the orange or brick-red precipitate with *hydrogen sulphide*, which is soluble in a solution of ammonium sulphide, and again precipitated by an acid.

Antimonious chloride, as already observed, is decomposed by *water*, yielding a precipitate of oxychloride. The precipitate dissolves in hydrochloric acid, and the resulting solution gives, with *potash*, a white precipitate of trioxide, soluble in a large excess of the reagent; with *ammonia* the same, insoluble in excess; with *potassium* or *sodium carbonate*, also a precipitate of trioxide, which dissolves in excess, especially of the potassium salt, but reappears after a while. If, however, the solution contains *tartaric acid*, the precipitate formed by potash dissolves easily in excess of the alkali; ammonia forms but a slight precipitate, and the precipitates formed by alkaline carbonates are insoluble in excess. The last mentioned characters are likewise exhibited by a solution of tartar-emetic (potassio-antimonious tartrate). *Zinc* and *iron* precipitate antimony from its solutions as a black powder. *Copper* precipitates it as a shining metallic film, which may be dissolved off by potassium permanganate, yielding a solution which will give the characteristic red precipitate with hydrogen sulphide.

Solid antimony-compounds, fused upon charcoal with sodium carbonate or potassium cyanide, yield a brittle globule of antimony, a thick white fume being at the same time given off, and the charcoal covered to some distance around with a white deposit of oxide.

Besides its application to medicine, antimony is of great importance in the arts, inasmuch as, in combination with lead, it forms *type-metal*. This alloy expands at the moment of solidifying, and takes an exceeding sharp impression of the mould. It is remarkable that both its constituents shrink under similar circumstances, and make very bad castings.

Britannia metal is an alloy of 9 parts tin and 1 part antimony, frequently also containing small quantities of copper, zinc, or bismuth. An alloy of 12 parts tin, 1 part antimony, and a small quantity of copper, forms a superior kind of pewter. Alloys of antimony with tin, or tin and lead, are now much used for machinery-bearings in place of gun-metal. Alloys of antimony with nickel and with silver occur as natural minerals.

Antimony trisulphide enters into the composition of the blue signal-lights used at sea.*

* Blue or Bengal light:

| | | |
|-----------------------|-----------|----------|
| Dry potassium nitrate | | 6 parts. |
| Sulphur | | 2 " |
| Antimony trisulphide | | 1 part. |

ALL in fine powder, and intimately mixed

ARSENIC.

Atomic weight, 75. Symbol, As.

ARSENIC is sometimes found native: it occurs in considerable quantity as a constituent of many minerals, combined with metals, sulphur and oxygen. In the oxidized state, it has been found in very minute quantity in a great many mineral waters. The largest proportion is derived from the roasting of natural arsenides of iron, nickel, and cobalt. The operation is conducted in a reverberatory furnace, and the volatile products are condensed in a long and nearly horizontal chimney, or in a kind of tower of brickwork, divided into numerous chambers. The crude arsenious oxide thus produced is purified by sublimation, and then heated with charcoal in a retort; the metal is reduced, and readily sublimes.

Arsenic has a steel-gray color, and high metallic lustre: it is crystalline and very brittle; it tarnishes in the air, but may be preserved unchanged in pure water. Its density, in the solid state, is 5.7 to 5.9. When heated, it volatilizes without fusion, and, if air be present, oxidizes to arsenious oxide. Its vapor-density, compared with that of hydrogen, is 150, which is twice its atomic weight, so that its molecule in the gaseous state, like that of phosphorus, occupies only half the volume of a molecule of hydrogen (p. 228). The vapor has the odor of garlic.

Arsenic combines with metals in the same manner as sulphur and phosphorus, which it resembles, especially the latter, in many respects: indeed, it is often regarded as a metalloïd.

Arsenic, like nitrogen, behaves in most respects as a triad element, not being capable of uniting with more than three atoms of any one monad element. Thus it forms the compounds AsH_3 , AsCl_3 , AsBr_3 , etc., but no compound analogous to the pentachloride of phosphorus or antimony. But just as ammonia, NH_3 , can take up the elements of hydrochloric acid to form sal-ammoniac, NH_4Cl , in which nitrogen appears quinquivalent, so likewise can arsenetted hydrogen or arsine, AsH_3 , unite with the chlorides, bromides, etc., of the radicles, methyl, ethyl, etc., to form salts in which the arsenic appears to be quinquivalent, e. g. :—



In like manner, arsenotrimethyl, $\text{As}(\text{CH}_3)_3$, unites with the chlorides of methyl and ethyl, forming the compounds $\text{As}(\text{CH}_3)_4\text{Cl}$ and $\text{As}(\text{CH}_3)_4(\text{C}_2\text{H}_5)\text{Cl}$.

Arsenic likewise forms two oxides, viz.: arsenious oxide, As_2O_3 , and arsenic oxide, As_2O_5 , with corresponding acids and salts, analogous to the phosphorous and phosphoric compounds: the arsenites, in particular, are isomorphous with the orthophosphates, and resemble them closely in many other respects.

Arsenious Chloride, AsCl_3 .—This, the only known chloride of arsenic, is produced, with omission of heat and light, when powdered arsenic is thrown into chlorine gas. It is prepared by distilling a mixture of 1 part of metallic arsenic and 6 parts of corrosive sublimate, and by distilling arsenious oxide with strong hydrochloric acid, or with a mixture of common salt and sulphuric acid. It is a colorless, volatile, highly poisonous liquid, decomposed by water into arsenious and hydrochloric acids. *Arsenous iodide*, AsI_3 , is formed by heating metallic arsenic with iodine: it is a deep red crystalline substance, capable of sublimation. The corresponding *arsenide and fluoride* are both liquid.

Hydrides.—Arsenic forms two hydrides, containing 2 and 3 atoms of hydrogen combined with 1 atom of arsenic.

The *trihydride*, *Arsenious hydride*, *Arsenettel hydrogen* or *Arsine*, AsH_3 , analogous in composition to ammonia, phosphine, and stibine, is obtained pure by the action of strong hydrochloric acid on an alloy of equal parts of zinc and arsenic, and is produced in greater or lesser proportion whenever hydrogen is set free in contact with arsenious acid. Arsenettel hydrogen is a colorless gas, of specific gravity 2.695, slightly soluble in water, and having the smell of garlic. It burns, when kindled, with a blue flame, generating arsenious acid. It is also decomposed by transmission through a red-hot tube. Many metallic solutions are precipitated by this substance. When inhaled, it is exceedingly poisonous, even in very minute quantity.

The *dihydride*, AsH_2 , or rather $\text{As}_2\text{H}_4 = \begin{array}{c} \text{AsH}_2 \\ | \\ \text{AsH}_2 \end{array}$, is produced by passing an electric current through water, the negative pole being formed of metallic arsenic; also when potassium or sodium arsenide is dissolved in water. It is a brown powder, which gives off hydrogen when heated in a close vessel, and burns when heated in the air. It is analogous in composition to arsenidimethyl or cacodyl, $\text{As}_2(\text{CH}_3)_4$.

Arsenious Oxide, Acid, and Salts.—*Arsenious oxide*, As_2O_3 , also called *white oxide of arsenic*, is produced in the manner already mentioned. It is commonly met with in the form of a heavy, white, glassy-looking substance, with smooth conchoidal fracture, having evidently undergone fusion. When freshly prepared it is often transparent, but by keeping becomes opaque, at the same time slightly diminishing in density, and acquiring a greater degree of solubility in water. 100 parts of that liquid dissolve at 100° about 11.5 parts of the opaque variety: the larger portion separates, however, on cooling, leaving about three parts dissolved: the solution, which contains *arsenious acid*, feebly reddens litmus. Cold water, agitated with powdered arsenious oxide, takes up a still smaller quantity. Alkalies dissolve this substance freely, forming arsenites; compounds with ammonia, baryta, strontia, lime, magnesia, and manganous oxide also have been formed: the silver salt is a beautiful lemon-yellow precipitate. The arsenites are, however, very unstable. Those which have the composition M_2AsO_3 , or $3\text{M}_2\text{O} \cdot \text{As}_2\text{O}_3$, are regarded as normal salts; there are also arsenites containing $\text{M}_4\text{As}_2\text{O}_5$, or $2\text{M}_2\text{O} \cdot \text{As}_2\text{O}_3$, and MAsO_2 , or $\text{M}_2\text{O} \cdot \text{As}_2\text{O}_3$, besides acid salts. Arsenious oxide is easily soluble in hot hydrochloric acid. Its vapor is colorless and inodorous, and it crystallizes on solidifying in brilliant transparent octohedrons. The oxide or acid itself has a feeble sweetish and astringent taste, and is a most fearful poison.

Arsenic Oxide, Acid and Salts.—When powdered arsenious oxide is dissolved in hot hydrochloric acid, and oxidized by the addition of nitric acid, the latter being added as long as red vapors are produced, the whole then cautiously evaporated to complete dryness, and the residue heated to low redness, arsenic oxide, As_2O_5 , remains in the form of a white anhydrous mass which has no action upon litmus. When strongly heated, it is resolved into arsenious oxide and free oxygen. In water it dissolves slowly but completely, giving a highly acid solution, which, on being evaporated to a syrupy consistence, deposits, after a time, hydrated crystals of arsenic acid, containing $2\text{H}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$, or $3\text{H}_2\text{O} \cdot \text{As}_2\text{O}_5 + \text{Aq}$. These crystals, when heated to 100° , give off their water of crystallization and leave *trihydric arsenate*, H_3AsO_4 , or $3\text{H}_2\text{O} \cdot \text{As}_2\text{O}_5$; at 140° – 160° , *dihydric arsenate*, $\text{H}_2\text{As}_2\text{O}_7$, or $2\text{H}_2\text{O} \cdot \text{As}_2\text{O}_5$, is left; and at 260° , *monohydric arsenate*, HAsO_3 , or $\text{H}_2\text{O} \cdot \text{As}_2\text{O}_5$. The aqueous solutions of the three hydrates and of the anhydrous oxide exhibit exactly the same characters, and all con-

tain trihydric arsenate, the other hydrates being immediately converted into that compound when dissolved in water; in this respect the hydrates of arsenic oxide differ essentially from those of phosphoric oxide (p. 217).

Arsenic acid is a very powerful acid, forming salts isomorphous with the corresponding phosphates: it is also tribasic. A sodium arsenate, $\text{Na}_3\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$, undistinguishable in appearance from common sodium phosphate, may be prepared by adding the carbonate to a solution of arsenic acid, until an alkaline reaction is apparent, and then evaporating. This salt also crystallizes with 7 molecules of water. Another arsenate, $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$, is produced when sodium carbonate in excess is fused with arsenic acid, or when the preceding salt is mixed with caustic soda. A third, $\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$, is made by substituting an excess of arsenic acid for the solution of alkali. The alkaline arsenates which contain basic water lose the latter at a red heat, but, unlike the phosphates, recover it when again dissolved. The arsenates of the alkalis are soluble in water: those of the earths and other metallic oxides are insoluble, but are dissolved by acids. The precipitate with silver nitrate is highly characteristic of arsenic acid: it is reddish-brown.

Sulphides.—Two sulphides of arsenic are known. The disulphide, As_2S_2 , occurs native as *Realgar*. It is formed artificially by heating arsenic acid with the proper proportion of sulphur. It is an orange-red, fusible, and volatile substance, employed in painting, and by the pyrotechnist in making *white fire*. The trisulphide or arsenious sulphide, As_2S_3 , also occurs native as *Orpiment*, and is prepared artificially by fusing arsenic with the appropriate quantity of sulphur, or by precipitating a solution of arsenious acid with hydrogen sulphide. It is a golden-yellow, crystalline substance, fusible, and volatile by heat. A cold solution of arsenic acid is not immediately precipitated by hydrogen sulphide, but after some hours the solution, saturated with hydrogen sulphide, yields a light yellow deposit of sulphur, the arsenic acid being reduced to arsenious acid, which is then gradually converted into lemon-yellow arsenious sulphide. In boiling solutions the precipitation takes place immediately. The mixture of sulphur and trisulphide thus produced, was formerly regarded as a pentasulphide analogous to arsenic acid.

The disulphide and trisulphide of arsenic are sulphur-acids uniting with other metallic sulphides to form sulphur salts. Those of the disulphide are called hyposulpharsenites; they are but little known. The salts of arsenious sulphide are called sulpharsenites. Their composition may be represented by that of the potassium salts, viz., KAsS_2 , or $\text{K}_2\text{S} \cdot \text{As}_2\text{S}_3$; $\text{K}_4\text{As}_2\text{S}_5$, or $2\text{K}_2\text{S} \cdot \text{As}_2\text{S}_3$; and K_3AsS_4 , or $3\text{K}_2\text{S} \cdot \text{As}_2\text{S}_3$. Of these the bibasic salts are the most common. The sulpharsenites of the alkali-metals and alkaline earth-metals are soluble in water, and may be prepared by digesting arsenious sulphide in the solutions of the corresponding hydrates or sulphhydrates; the rest are insoluble, and are obtained by precipitation. Sulphur salts, called sulpharsenates, analogous in composition to the arsenates, are produced, in like manner, by digesting the mixture of sulphur and arsenious sulphide precipitated, as above mentioned, from arsenic acid, in solutions of alkaline hydrates or sulphhydrates; also by passing gaseous hydrogen sulphide through solutions of arsenates. There are three sulpharsenates of potassium, containing, KAsS_4 , or $\text{K}_2\text{S} \cdot \text{As}_2\text{S}_5$; $\text{K}_4\text{As}_2\text{S}_7$, or $2\text{K}_2\text{S} \cdot \text{As}_2\text{S}_5$; and K_3AsS_6 , or $3\text{K}_2\text{S} \cdot \text{As}_2\text{S}_5$. The sulpharsenates of the alkali metals and alkaline earth metals are soluble in water; the rest are insoluble, and are obtained by precipitation.

Arsenious acid is distinguished by characters which cannot be misunderstood.

Silver nitrate, mixed with a solution of arsenious acid in water, occasions no precipitate, or merely a faint cloud: but if a little fixed alkali, or a drop of ammonia, be added, a yellow precipitate of silver arsenite immediately falls. The precipitate is exceedingly soluble in excess of ammonia; that liquid must, therefore, be added with great caution; it is likewise very soluble in nitric acid.

Copper sulphate gives no precipitate with solution of arsenious acid, until the addition has been made of a little alkali, when a brilliant yellow-green precipitate (Scheele's green) falls, which also is very soluble in excess of ammonia.

Hydrogen sulphide, passed into a solution of arsenious acid, to which a few drops of hydrochloric or sulphuric acid have been added, throws down a copious bright yellow precipitate of orpiment, which is easily dissolved by ammonia, and reprecipitated by acids.

Solid arsenious oxide, heated by the blow-pipe in a narrow glass tube with small fragments of dry charcoal, affords a sublimate of metallic arsenic in the shape of a brilliant steel-gray metallic ring. A portion of this, detached by the point of a knife, and heated in a second glass tube, with access of air, yields, in its turn, a sublimate of colorless, transparent, octohedral crystals of arsenious oxide.

All these experiments, which jointly give demonstrative proof of the presence of the substance in question, may be performed with perfect precision and certainty upon exceedingly small quantities of material.

The detection of arsenious acid in complex mixtures, containing organic matter and common salt, as beer, gruel, soup, etc., or the fluid contents of the stomach in cases of poisoning, is a far more difficult problem, but one which is, unfortunately, often required to be solved. These organic matters interfere completely with the liquid tests, and render their indications worthless. Sometimes the difficulty may be eluded by a diligent search in the suspected liquid, and in the vessel containing it, for fragments or powder of solid arsenious oxide, which, from its small degree of solubility, often escape solution, and from the high density of the substance, may be found at the bottom of the vessels in which the fluids are contained. If anything of the kind be found, it may be washed by decantation with a little cold water, dried, and then reduced with charcoal. For the latter purpose, a small glass tube is taken, having the figure represented in the margin; white German glass, free from lead, is to be preferred. The arsenious oxide, or what is suspected to be such, is dropped to the bottom, and covered with splinters or little fragments of charcoal, the tube being filled to the shoulder. The whole is gently heated, to expel any moisture that may be present in the charcoal, and the deposited water wiped from the interior of the tube with bibulous paper. The narrow part of the tube containing the charcoal, from *a* to *b*, is now heated by the blow pipe flame; when red hot, the tube is inclined, so that the bottom also may become heated. The arsenious oxide, if present, is vaporized, and reduced by the charcoal, and a ring of metallic arsenic deposited on the cool part of the tube. To complete the experiment, the tube may be melted at *a* by the point of the flame, drawn off, and closed, and the arsenic oxidized to arsenious oxide, by chasing it up and down by the heat of a small spirit-lamp. A little water may afterwards be introduced, and boiled in the tube, by which arsenious oxide will be dissolved, and to this solution the tests of silver nitrate and ammonia, copper sulphate and ammonia, and hydrogen sulphide, may be applied.

Fig. 167.



When the search for solid arsenious oxide fails, the liquid itself must be examined; a tolerably lumpid solution must be obtained, from which the arsenic may be precipitated by hydrogen sulphide, and the orpiment collected, and reduced to the metallic state. It is in the first part of this operation that the chief difficulty is found: such organic mixtures refuse to filter, or filter so slowly as to render some method of acceleration indispensable.* Boiling with a little caustic potash or acetic acid will sometimes effect this object. The following is an outline of a plan which has been found successful in a variety of cases in which a very small quantity of arsenious acid had been purposely added to an organic mixture: Oil of vitriol, itself perfectly free from arsenic, is mixed with the suspected liquid, in the proportion of about a measured ounce to a pint, having been previously diluted with a little water, and the whole is boiled in a flask for half an hour, or until a complete separation of solid and liquid matter becomes manifest. The acid converts any starch that may be present into dextrin and sugar: it completely coagulates albuminous substances, and casein, in the case of milk, and brings the whole in a very short time into a state in which filtration is both easy and rapid. Through the filtered solution, when cold, a current of hydrogen sulphide is transmitted, and the liquid is warmed, to facilitate the deposition of the arsenious sulphide, which falls in combination with a large quantity of organic matter, which often communicates to it a dirty color. This is collected upon a small filter, and washed. It is next transferred to a capsule, and heated with a mixture of nitric and hydrochloric acids, by which the organic impurities are in great measure destroyed, and the arsenic oxidized to arsenic acid. The solution is evaporated to dryness, the soluble part taken up by dilute hydrochloric acid, and then the solution saturated with sulphurous acid, whereby the arsenic acid is reduced to the state of arsenious acid, the sulphurous being oxidized to sulphuric acid. The solution of arsenious acid, may now be precipitated by hydrogen sulphide without any difficulty. The liquid is warmed, and the precipitate washed by decantation, and dried. It is then mixed with *black flux*, and heated in a small glass tube, similar to that already described, with similar precautions: a ring of reduced arsenic is obtained, which may be oxidized to arsenious oxide, and further examined. The *black flux* is a mixture of potassium carbonate and charcoal, obtained by calcining cream of tartar in a close crucible; the alkali transforms the sulphide into arsenious acid, the charcoal subsequently effecting the deoxidation. A mixture of anhydrous sodium carbonate and charcoal may be substituted with advantage for the common *black flux*, as it is less hygroscopic.

Other methods of proceeding, different in principle from the foregoing, are also employed, as that of the late Mr. Marsh, which is exceedingly delicate. The suspected liquid is acidulated with sulphuric acid, and placed in contact with metallic zinc; the hydrogen reduces the arsenious acid and combines with the arsenic, if any be present. The gas is burned at a jet, and a piece of glass or porcelain held in the flame, when any admixture of arsenetted hydrogen is at once known by the production of a brilliant black metallic spot of reduced arsenic on the porcelain; or the gas is passed through a glass tube heated at one or two places to redness, whereby the arsenetted hydrogen is decomposed, a ring of metallic arsenic appearing behind the heated portion of the tube.

It has been observed (page 389) that antimonetted hydrogen gives a similar result. In order to distinguish the two substances, the gas may be passed into a solution of silver nitrate. Both gases give rise to a black precipitate, which, in the case of antimonetted hydrogen, consists of silver

* Respecting the separation of the arsenious acid by dialysis, see page 164.

antimonide, Ag.Sb , whilst in the case of arsenetted hydrogen, it is pure silver, the arsenic being then converted into arsenious acid, which combines with a portion of silver oxide. The silver arsenite remains dissolved in the nitric acid which is liberated by the precipitation of the silver, and may be thrown down with its characteristic yellow color by adding ammonia to the liquid filtered off from the black precipitate. The black silver antimonide, when carefully washed, and subsequently boiled with a solution of tartaric acid, yields a solution containing antimony only, from which hydrogen sulphide separates the characteristic orange-yellow precipitate of antimonious sulphide.

A convenient form of Marsh's instrument is that shown in fig. 158: it consists of a bent tube, having two bulbs blown upon it, fitted with a stopcock and narrow jet. Shps of zinc are put into the lower bulb, which is afterwards filled with the liquid to be examined. On replacing the stopcock, closed, the gas collects and forces the liquid into the upper bulb, which then acts by its hydrostatic pressure, and expels the gas through the jet so soon as the stopcock is opened. It must be borne in mind that both common zinc and sulphuric acid often contain traces of arsenic. Professor Bloxam* has proposed an important modification of Marsh's process for the detection of arsenic and antimony in organic substances, which is based on the behavior of solutions of these metals under the influence of the electric current. Antimony is deposited in the metallic state, without any disengagement of antimonetted hydrogen, while arsenic is evolved as arsenetted hydrogen, which may be recognized by the characters already indicated.

A shp of copper-foil boiled in the poisoned liquid, previously acidulated with hydrochloric acid, withdraws the arsenic, and becomes covered with a white alloy. By heating the metal in a glass tube, the arsenic is expelled, and oxidized to arsenious acid. This is called Reinsch's test.

Fig 158.



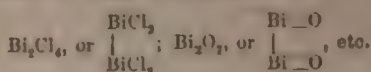
BISMUTH.

Atomic weight, 210. Symbol, Bi .

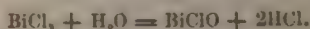
BISMUTH is found chiefly in the metallic state, disseminated through various rocks, from which it is separated by simple exposure to heat. The metal is highly crystalline and very brittle: it has a reddish-white color, and a density of 9.9. Crystals of great beauty may be obtained by slowly cooling a considerable mass of this substance until solidification has commenced, then piercing the crust, and pouring out the fluid residue. Bismuth melts at about 260°C . (500°F .), and volatilizes at a high temperature. It is remarkable as being the most diamagnetic of all known bodies. It is little oxidized by the air, but burns with a bluish flame when strongly heated. Nitric acid somewhat diluted dissolves it freely.

Bismuth forms three classes of compounds, in which it is bi-, tri-, and quinquivalent respectively. The tri-compounds are the most stable and

the most numerous. The only known compounds in which bismuth is quinquivalent are indeed the pentoxide, Bi_2O_5 , together with the corresponding acid and metallic salts. Nevertheless, bismuth is regarded as a pentad, on account of the analogy of its compounds with those of antimony. Several bismuth compounds are known in which the metal is apparently bivalent, but really trivalent, as:—



Chlorides.—The *trichloride*, or *Bismuthous chloride*, is formed when bismuth is heated in a current of chlorine gas, and passes over as a white, easily fusible substance, which readily attracts moisture from the air, and is converted into a crystallized hydrate. The same substance is produced when bismuth is dissolved in nitro-muriatic acid, and the solution evaporated. Bismuthous chloride dissolves in water containing hydrochloric acid, but is decomposed by pure water, yielding a white precipitate of oxychloride —



The *dichloride*, Bi_2Cl_4 , produced by heating the trichloride with metallic bismuth, is a brown, crystalline, easily fusible mass, decomposed by water. At a high temperature it is resolved into the trichloride and metallic bismuth.

Oxides.—The *trioxide*, or *Bismuthous oxide*, is a straw-yellow powder, obtained by gently igniting the neutral or basic nitrate. It is fusible at a high temperature, and in that state acts towards siliceous matter as a powerful flux.

The *hydrate*, $\text{Bi}(\text{HO})_3$ or $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is obtained as a white precipitate when a solution of the nitrate is decomposed by an alkali. Both the hydrate and the anhydrous oxide dissolve in the stronger acids, forming the bismuthous salts, which have the composition BiR_3 , where R denotes an acid radicle, *e. g.*, BiCl_3 , $\text{Bi}(\text{NO}_3)_3$, $\text{Bi}(\text{SO}_4)_3$. Many of these salts crystallize well, but cannot exist in solution unless an excess of acid is present. On diluting the solutions with water, a basic salt is precipitated, and an acid salt remains in solution.

The *normal nitrate*, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, or $\text{Bi}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$, forms large transparent colorless crystals, which are decomposed by water in the manner just mentioned, yielding an acid solution containing a little bismuth, and a brilliant white crystalline powder, which varies to a certain extent in composition according to the temperature and the quantity of water employed, but frequently consists of a basic nitrate, $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, or $\text{Bi}(\text{NO}_3)_2 \cdot \text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. A solution of bismuth nitrate, free from any great excess of acid, poured into a large quantity of cold water, yields an insoluble basic nitrate, very similar in appearance to the above, but containing rather a larger proportion of bismuth oxide. This basic nitrate was once extensively employed as a cosmetic, but it is said to injure the skin, rendering it yellow and leather-like. It is used in medicine.

Bismuth pentoxide, or *Bismuthic oxide*, Bi_2O_5 .—When bismuth trioxide is suspended in a strong solution of potash, and chlorine passed through the liquid, decomposition of water ensues, hydrochloric acid being formed, and the trioxide being converted into the pentoxide. To separate any trioxide that may have escaped oxidation, the powder is treated with dilute nitric acid, when the bismuthic oxide is left as a reddish powder, which is insoluble in water. This substance combines with bases, but the compounds

are not very well known. According to Arppe, there is an acid potassium bismuthate containing Bi_7KHO_6 , or $2\text{Bi}_4\text{O}_5 \cdot \begin{cases} \text{K}_2\text{O} \\ 11\text{H}_2\text{O} \end{cases}$. The pentoxide when heated loses oxygen, an intermediate oxide, Bi_2O_4 , being formed, which may be considered as *bismuthous bismuthate*, $2\text{Bi}_4\text{O}_5 = \text{Bi}_2\text{O}_5 \cdot \text{Bi}_2\text{O}_4$.

Bismuth is sufficiently characterized by the decomposition of its nitrate and chloride by water, and by the black precipitate of bismuth sulphide, insoluble in ammonium sulphide, which its solutions yield when exposed to the action of hydrogen sulphide.

A mixture of 8 parts of bismuth, 5 parts of lead, and 3 of tin, is known under the name of *fusible metal*, and is employed in taking impressions from dies and for other purposes: it melts below 100° .

Bismuth is used, in conjunction with antimony, in the construction of thermo-electric piles, these two metals forming the opposite extremes of the thermo-electric series.

VANADIUM.

Atomic weight, 51.2. Symbol, V.

VANADIUM is found, in small quantity, in some iron ores, also as *vanadate of lead*. It has likewise been discovered in the iron slag of Staffordshire, and recently, by Roseoe,* in larger quantity in the copper-bearing beds at Alderly Edge and Mottram St. Andrews, in Cheshire. Metallic vanadium is obtained by prolonged ignition of the dichloride in pure dry hydrogen, as a grayish-white powder, appearing under the microscope as a crystalline mass, with a strong silver-white lustre. It is non-volatile, decomposes water at 100° , does not tarnish in the air, burns with brilliant scintillations when thrown into a flame; burns vividly when quickly heated in oxygen, forming the pentoxide; is insoluble in hydrochloric acid; dissolves slowly in hydrofluoric acid with evolution of hydrogen, rapidly in nitric acid, forming a blue solution. In a current of chlorine it takes fire, and is converted into the tetrachloride.

Vanadium was, till lately, regarded as a hexad metal, analogous to tungsten and molybdenum; but Roseoe has shown that it is a pentad, belonging to the phosphorus and arsenic group. This conclusion is based upon the composition of the oxides and oxychlorides; and on the isomorphism of the vanadates with the phosphates.

Vanadium Oxides.—Vanadium forms five oxides, represented by the formulae, V_2O , V_2O_2 , V_2O_3 , V_2O_4 , V_2O_5 , analogous, therefore, to the oxides of nitrogen.

The *monoxide*, V_2O , is formed by prolonged exposure of metallic vanadium to the air at ordinary temperatures, more quickly at a dull red heat. It is a brown substance, which, when heated in the air, is gradually converted into the higher oxides.

The *dioxide*, V_2O_2 , which was regarded by Berzelius as metallic vanadium, is obtained by reducing either of the higher oxides with potassium, or by passing the vapor of vanadium oxytrichloride (VOCl_3), mixed with excess of hydrogen, through a combustion tube containing red-hot charcoal. As obtained by the second process, it forms a light-gray glittering powder, or a metallicallly lustrous crystalline crust, having a specific gravity of 3.64,

* Proceedings of the Royal Society, xvi. 223.

brittle, very difficult to fuse, and a conductor of electricity. When heated to redness in the air, it takes fire and burns to black oxide. It is insoluble in sulphuric, hydrochloric, and hydrofluoric acid, but dissolves easily in nitromuriatic acid, forming a dark-blue liquid.

The dioxide may be prepared in solution by the action of nascent hydrogen (evolved by metallic zinc, cadmium, or sodium-amalgam) on a solution of vanadic acid in sulphuric acid. After passing through all shades of blue and green, the liquid acquires a permanent lavender tint, and then contains the vanadium in solution as dioxide, or as hypovanadious salt. This compound absorbs oxygen more rapidly than any other known agent, and bleaches indigo and other vegetable colors as quickly as chlorine.

Vanadium dioxide may be regarded as entering into many vanadium compounds, as a bivalent radicle (just like uranyl in the uranic compounds), and may therefore be called *vanadyl*.

Vanadium trioxide, V_2O_3 , or *Vanadylmonoxide*, $(V_2O_3)^{10}O$, is obtained by igniting the pentoxide in hydrogen gas, or in a crucible lined with charcoal. It is a black powder, with an almost metallic lustre, and infusible; by pressure it may be united into a coherent mass which conducts electricity. When exposed warm to the air, it glows, absorbs oxygen, and is converted into pentoxide. At ordinary temperatures, it slowly absorbs oxygen, and is converted into tetroxide. By ignition in chlorine gas it is converted into vanadyl trichloride and vanadium pentoxide. It is insoluble in acids, but may be obtained in solution by the reducing action of nascent hydrogen (evolved from metallic magnesium) on a solution of vanadic acid in sulphuric acid.

Vanadium tetroxide, *Hypovanadic oxide*, or *Vanadyl dioxide*, $V_2O_4 = (V_2O_3)O_2$.—This oxide is produced, either by oxidation of the dioxide or trioxide, or by partial reduction of the pentoxide; also by heating hypovanadic chloride, $V_2O_4Cl_2$, to redness in an atmosphere of carbon dioxide.* By allowing the trioxide to absorb oxygen at ordinary temperatures, the tetroxide is obtained in blue shining crystals. It dissolves in acids, the more easily in proportion as it has been less strongly ignited, forming solutions of hypovanadic salts, which have a bright blue color. The same solutions are produced by the action of moderate reducing agents, such as sulphurous, sulphydric, or oxalic acid, upon vanadic acid in solution; also by passing air through acid solutions of the dioxide till a permanent blue color is attained. With the *hydrates* and *normal carbonates of the fixed alkalis*, they form a grayish-white precipitate of hydrated oxide, $V_2O_4 \cdot 11H_2O$, which dissolves in a moderate excess of the reagent, but is reprecipitated by a large excess in the form of a vanadite of the alkali metal.

Ammonia in excess produces a brown precipitate, soluble in pure water, but insoluble in water containing ammonia.—*Ammonium sulphide* forms a black-brown precipitate, soluble in excess.—*Tincture of galls* forms a finely divided black precipitate, which gives to the liquid the appearance of ink.

Hypovanadic trisulphate, $V_2O_4 \cdot 3SO_3 + 6H_2O$, is obtained as a blue deliquescent crystalline powder by dissolving vanadic oxide in strong sulphuric acid and reducing the solution with sulphurous acid. A salt of similar character, containing $4H_2O$, is obtained by precipitating the concentrated solution with strong sulphuric acid. A *disulphate*, $V_2O_4 \cdot 2SO_3 + 7H_2O$, is obtained as a light-blue crystalline powder, when the pure trisulphate, or the residue left on evaporating a solution of the tetroxide in sulphuric acid, is treated with absolute alcohol (Crow). Berzelius by similar means obtained a disulphate with $4H_2O$.

Vanadium tetroxide also unites with the more basic metallic oxides,

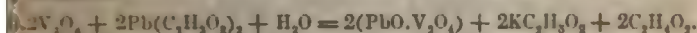
* J. K. Crow, Chem. Soc. Journ., 1876, II.

ing salts called hypovanadates, all of which are insoluble, except those of the alkali-metals. The solutions of the alkaline hypovanadates are brown, but when treated with *hydrogen sulphide* they acquire a splendid red-purple color, arising from the formation of a sulphur salt. *Acids* color them blue, by forming a double hypovanadic salt; *tincture of gall* colors them blackish-blue. The insoluble hypovanadates, when exposed or covered with water, become green, and are converted into vanadates.

Rose has obtained the following hypovanadates by treating hypovanadic oxide with the corresponding bases:—

| | | |
|--------------------------|---------------------|-------------|
| Potassium salt | $K_2O.2V_2O_5$ | + $7H_2O$ |
| Sodium salt | $Na_2O.2V_2O_5$ | + $7H_2O$ |
| Ammonium salt | $(NH_4)_2O.2V_2O_5$ | + $3H_2O$ |
| Barium salt | $BaO.2V_2O_5$ | + $5H_2O$. |

The *lead salt*, $PbO.V_2O_5$, is formed, together with potassium acetate and acetic acid, by precipitating a solution of lead acetate with potassium hypovanadate:



The *silver salt*, $Ag_2O.V_2O_5$, is formed by a precisely similar reaction from potassium hypovanadate and silver nitrate.

Vanadium pentoxide, *Vanadic oxide*, or *Vanadyl trioxide*, $V_2O_5 = (V_2O_7)O_3$, this is the highest oxide of vanadium. It may be prepared from native vanadate. This mineral is dissolved in nitric acid, and the lead and acid are precipitated by hydrogen sulphide, which at the same time fuses the vanadium pentoxide to tetroxide. The blue filtered solution then evaporated to dryness, and the residue digested in ammonia, which solves out the vanadic oxide reproduced during evaporation. In this action a lump of sal-ammoniac is put; as that salt dissolves, ammonium acetate subsides as a white powder, being scarcely soluble in a saturated solution of ammonium chloride. By exposure to a temperature below 100° in an open crucible, the ammonia is expelled, and vanadic oxide is left. By a similar process, Rose has prepared vanadic oxide from a lime sulphate containing 2 per cent. of vanadium, obtained in working up a cobalt ore from Mottram in Cheshire.

Vanadium pentoxide has a reddish-yellow color, and dissolves in 1000 pts. of water, forming a light yellow solution. It dissolves also in stronger acids, forming red or yellow solutions, some of which yield crystalline compounds (vanadic salts) by spontaneous evaporation. It unites, however, with bases more readily than with acids, forming salts called *vanadates*. When fused with alkaline carbonates, it eliminates 3 molecules of carbon dioxide, forming *orthovanadates* analogous to the orthophosphates; viz.:



It also forms *metavanadates* and *pyrovanadates* analogous to the meta- and pyro-phosphates, and two series of acid vanadates or *anhydrovanadates*, viz.:

| | | |
|----------------------------------|----------------------|--------------------|
| Lead orthovanadate | $Pb_2(VO_4)_2$ | or $3PbO.V_2O_5$ |
| Barium pyrovanadate | $Ba_2V_2O_7$ | or $2BaO.V_2O_5$ |
| Strontium metavanadate | $Sr(VO_4)_2$ | or $SrO.V_2O_5$ |
| Strontium divanadate | $Sr(VO_4)_2.V_2O_5$ | or $SrO.2V_2O_5$ |
| Strontium trivanadate | $Sr(VO_4)_2.2V_2O_5$ | or $SrO.3V_2O_5$. |

Lead metavanadate occurs native as *dechenite*; the orthovanadate also, obtained with lead chloride, as *vanadinite* or *vanadite*, $PbCl_2.3Pb_3(VO_4)_2$.

the mineral in which vanadium was first discovered. *Deschloizite* is a plumbic vanadate, $Pb_2V_2O_7$, or $2PbO.V_2O_5$, analogous in composition to pyrophosphate.

The metavanadates are mostly yellow; some of them, however, especially those of the alkaline earth metals, and of zinc, cadmium, and lead, are converted by warming—either in the solid state, or under water, or in aqueous solution, especially in presence of a free alkali or alkaline carbonate—into isomeric colorless salts. The same transformation takes place also, though more slowly, at ordinary temperatures. The metavanadates of alkali-metal are colorless. The acid vanadates are yellow, or yellowish-red, both in the solid state and in solution: hence the solution of a neutral vanadate becomes yellowish-red on addition of an acid. The metavanadates of ammonium, the alkali-metals, barium, and lead, are but sparingly soluble in water; the other metavanadates are more soluble. The alkali vanadates are more soluble in pure water than in water containing free alkali or salt: hence they are precipitated from their solutions by addition of alkali in excess, or of salts. The vanadates are insoluble in alcohol. The aqueous solutions of vanadates form yellow precipitates with antimony, copper, lead, and mercury salts: with *tincture of galls* they form a deep blue liquid, which has been proposed for use as vanadium ink.

Hydrogen sulphide reduces them to hypovanadates, changing the color from red or yellow to blue, and forming a precipitate of sulphur.

Ammonium sulphide colors the solutions brown-red, and, on adding an acid, a light-brown precipitate is formed, consisting of vanadic sulphide mixed with sulphur, the liquid at the same time turning blue. *Hydrochloric acid* decomposes the vanadates, with evolution of chlorine and formation of vanadium tetroxide.

Vanadium Chlorides.—Three of these compounds have been obtained viz.: VCl_2 , VCl_3 , and VCl_4 .

The *tetrachloride*, VCl_4 , is formed when metallic vanadium or the monoxide is heated in a current of chlorine, or when the vapor of the oxytrichloride, $VOCl_3$, mixed with chlorine, is passed several times over red-hot charcoal. It is a dark yellowish-brown liquid, having a specific gravity of 1.8384 at 0° , boiling at 154° , not solidifying at 18° . Its vapour-density referred to hydrogen is 96.6, which is half the molecular weight

$(= \frac{51.5 + 4 \times 35.5}{2})$, showing that the molecule VCl_4 exhibits the normal

condensation to 2 volumes of vapor. The tetrachloride is quickly decomposed by water, forming a blue solution of vanadious acid. It does not take up bromine or an additional quantity of chlorine when heated there with in sealed tubes: hence it appears that vanadium does not readily form pentad compounds with the monatomic chlorous elements.

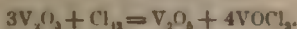
The *trichloride*, VCl_3 , obtained by decomposition of the tetrachloride slowly at ordinary temperatures, quickly at the boiling heat, crystallizes in peach-blossom-colored shining plates resembling chromic chloride. It is slowly decomposed by water, forming a green solution of hypovanadic acid.

The *dichloride*, VCl_2 , obtained by passing the vapor of the tetrachloride mixed with hydrogen through a red-hot tube, crystallizes in green micaceous plates, which are decomposed by water, forming a violet solution of hypovanadious acid.

Vanadium Oxychlorides, or Vanadyl Chlorides.—Four of these compounds are known, viz.: $VOCl_3$, $VOCl_2$, $VOCl$, and V_2O_7Cl .

The *oxytrichloride*, $VOCl_3$ (formerly regarded as vanadium trichloride), is prepared:

(1) By the action of chlorine on the trioxide:



(2) By burning the dioxide in chlorine gas, or by passing that gas over an ignited mixture of the trioxide, tetroxide, or pentoxide, and condensing the vapors in a cooled U-tube.

Vanadium oxytrichloride, or vanadyl trichloride, is a golden-yellow liquid of specific gravity 1.841 at 14.5°. Boiling-point, 127°. Vapor-density, by experiment, 6.108; by calculation, 6.119. When exposed to the air, it emits cinnabar-colored vapors, being resolved by the moisture of the air into hydrochloric and vanadic acids. It oxidizes magnesium and sodium. Its vapor, passed over perfectly pure carbon at a red heat, yields carbon dioxide; and when passed, together with hydrogen, through a red-hot tube, yields vanadium trioxide. These reactions show that the compound contains oxygen.

The other oxychlorides of vanadium are solid bodies obtained by partial reduction of the oxytrichloride with zinc or hydrogen.

The second, $VOCl_2$, or $V_2O_4Cl_4$ (hypovanadic chloride), is also produced by dissolving the pentoxide, with aid of heat, in hydrochloric acid, and reducing the green solution with sulphurous acid. The resulting blue liquid leaves, on evaporation over the water-bath, a brown deliquescent residue, which yields a blue solution with water (Crow).

The *tribromide*, VBr_3 , and the *oxybromides*, $VOBr_2$ and $VOBr_3$, have also been obtained. The first is a grayish-black amorphous solid; the second, a dark-red liquid; the third, a yellowish-brown deliquescent solid.

Vanadium Sulphides.—Two of these compounds are known, analogous to the tetroxide and pentoxide: both are sulphur acids. The *tetra-sulphide*, or *Vanadous sulphide*, V_2S_4 , is a black substance formed by heating the tetroxide to redness in a stream of hydrogen sulphide; also, as a hydrate, by dissolving a vanadous salt in excess of an alkaline monosulphide, and precipitating with hydrochloric acid. The *pentasulphide*, or *Vanadic sulphide*, V_2S_5 , is formed in like manner by precipitation from an alkaline vanadate.

Vanadium Nitrides.—The *mononitride*, VN , is formed by heating the compound of vanadium oxytrichloride with ammonium chloride to whiteness in a current of ammonia gas. It is a greenish-white powder, unalterable in the air. The *dinitride*, VN_2 , or V_2N_4 , is obtained by exposing the same double salt in ammonia gas to a moderate heat. It is a black powder strongly acted upon by nitric acid.

All vanadium compounds heated with borax or phosphorus-salt in the outer blow-pipe flame produce a clear bead, which is colorless if the quantity of vanadium is small, yellow when it is large; in the inner flame the bead acquires a beautiful green color.

Vanadic and chromic acids are the only acids whose solutions are red; they are distinguished from one another by the vanadic acid becoming blue, and the chromic acid green, by deoxidation.

When a solution of vanadic acid, or an acidulated solution of an alkaline vanadate, is shaken up with ether containing hydrogen dioxide, the aqueous solution acquires a red color, like that of ferric acetate, while the ether remains colorless. This reaction will serve to detect the presence of 1 part of vanadic acid in 40,000 parts of liquid. The other reactions of vanadium in solution have already been described.

TANTALUM.

Atomic weight, 182. Symbol, Ta.

This metal was discovered, in 1803, by Ekeberg, in two Swedish minerals, tantalite and yttrotantalite. A very similar metal, *columbium*, had been discovered in the preceding year by Hatchett, in columbite from Massachusetts; and Wollaston, in 1807, on comparing the compounds of these metals, concluded that they were identical, an opinion which was for many years received as correct; but their separate identity has been completely established by the researches of H. Rose (commenced in 1846), who gave to the metal from the American and Bavarian columbites the name *Niobium*, by which it is now universally known. More recently, Marignac has shown that nearly all tantalites and columbites contain both tantalum and niobium (or columbium), some tantalates, from Kinaito, in Finland, being, however, free from niobium, and some of the Greenland columbites containing only the latter metal unmixed with tantalum. In all these minerals tantalum exists as a tantalate of iron and manganese; yttrotantalite is essentially a tantalate of yttrium, containing also uranium, calcium, iron, and other metals. Tantalum is also contained in some varieties of wolfram.

Metallic tantalum is obtained by heating the fluotantalate of potassium or sodium with metallic sodium in a well-covered iron crucible, and washing out the soluble salts with water. It is a black powder, which, when heated in the air, burns with a bright light, and is converted, though with difficulty, into tantalic oxide. It is not attacked by sulphuric, hydrochloric, nitric, or even nitro-muriatic acid. It dissolves slowly in warm aqueous hydrofluoric acid, with evolution of hydrogen, and very rapidly in a mixture of hydrofluoric and nitric acids.

Tantalum, in its principal compounds, is quinquivalent, the formula of tantalic chloride being $TaCl_5$, that of tantalic fluoride, TaF_5 , and that of tantalic oxide (which, in combination with bases, forms the tantalates), Ta_2O_5 . There is also a tantalous oxide, said to have the composition TaO_2 , and a corresponding sulphide, TaS_2 .

Tantallic Chloride, $TaCl_5$, is obtained, as a yellow sublimate, by igniting an intimate mixture of tantalic oxide and charcoal in a stream of chlorine gas. It begins to volatilize at 144° , and melts to a yellow liquid at 221° . The vapor-density between 350° and 440° , has been found by Deville and Troost to be 12.42 referred to air, or 178.9 referred to hydrogen: by calculation, for the normal condensation to two volumes, it is 179.75. Tantallic chloride is decomposed by water, yielding hydrochloric and tantalic acids; but the decomposition is not complete even at the boiling heat.

Tantallic Fluoride, TaF_5 , is obtained in solution by treating tantalic hydrate with aqueous hydrofluoric acid. The solution, mixed with alkaline fluorides, forms soluble crystallizable salts, called tantalo fluorides, or fluotantalates. The potassium salt, TaK_2F_7 or $TaF_5 \cdot 2KF$, crystallizes in monoclinic prisms, isomorphous with the corresponding fluoniobate.

Tantallic Oxide, Ta_2O_5 , is produced when tantalum burns in the air, also by the action of water on tantalic chloride, and may be separated as a hydrate from the tantalates by the action of acids. It may be prepared from tantalite, which is a tantalate of iron and manganese, by fusing the

finely pulverized mineral with twice its weight of potassium hydroxide, digesting the fused mass in hot water, and supersaturating the filtered solution with hydrochloric or nitric acid: hydrated tantalic oxide is then precipitated in white flocks, which may be purified by washing with water.*

Anhydrous tantalic oxide, obtained by igniting the hydrate or sulphate, is a white powder, varying in density from 7.022 to 8.264, according to the temperature to which it has been exposed. Heated in ammonia gas it yields tantalum nitride: heated with carbon bisulphide, it is converted into tantalum bisulphide. It is insoluble in all acids, and can be rendered soluble only by fusion with potassium hydrate or carbonate.

Hydrated Tantalic oxide, or Tantalic acid, obtained by precipitating an aqueous solution of potassium tantalate with hydrochloric acid, is a snow-white bulky powder, which dissolves in hydrochloric and hydrofluoric acids: when strongly heated, it glows and gives off water.

Tantalum oxide unites with basic metallic oxides, forming the tantalates, which are represented by the formulae, $M_2O.Ta_2O_5$ and $4M_2O.3Ta_2O_5$, the first including the native tantalates, such as ferrous tantalate, and the second certain easily crystallizable tantalates of the alkali-metals. The tantalates of the alkali-metals are soluble in water, and are formed by fusing tantalic oxide with caustic alkalies: those of the earth-metals and heavy metals are insoluble, and are formed by precipitation.

Tantalum dioxide, or Tantalous oxide, TaO_2 , may be represented by the formula $\begin{array}{c} O^- - Ta - O \\ | \\ O - Ta - O \end{array}$, in which the metal is still quinquivalent. It is produced by exposing tantalic oxide to an intense heat by a crucible lined with charcoal. It is a hard dark gray substance, which, when heated in the air, is converted into tantalic oxide.

Hydrochloric or sulphuric acid, added in excess to a solution of alkaline tantalate, forms a precipitate of tantalic acid, which redissolves in excess of the hydrochloric, but not of the sulphuric acid. *Potassium ferrocyanide*, added to a very slightly acidulated solution of an alkaline tantalate, forms a yellow precipitate, the *ferriocyanide*, a white precipitate. *Infusion of galls* forms a light yellow precipitate, soluble in alkalies. When tantalic chloride is dissolved in strong sulphuric acid, and then water and metallic zinc are added, a fine blue color is produced, which does not turn brown, but soon disappears.

Tantalum oxide fused with microcosmic salt in either blowpipe flame forms a clear, colorless glass, which does not turn red on addition of a ferrous salt. With borax it also forms a transparent glass, which may be rendered opaque by interrupted blowing, or *flaming*.

NIOBIUM, or COLUMBIUM.

Atomic weight, 94. Symbol, Nb.

This metal, discovered in 1801 by Hatchett, in American columbite, exists likewise, associated with tantalum, in columbites from other sources, and in most tantalites; also, associated with yttrium, uranium, iron, and small quantities of other metals, in Siberian samarkite, uranotantalite, or yttriontantalite; also in pyrochlore, euxenite, and a variety of pitchblende from Hadersdalen in Norway.

* For more complete methods of preparation, see Watts's Dictionary of Chemistry, vol. i. p. 606.

The metal, obtained in the same manner as tantalum, is a black powder, which oxidizes with incandescence when heated in the air. It dissolves in hot hydrofluoric acid, with evolution of hydrogen, and, at ordinary temperatures, in a mixture of hydrofluoric and nitric acid; slowly, also, when heated with strong sulphuric acid. It is oxidized by fusion with acid potassium sulphate, and gradually converted into potassium niobate by fusion with potassium hydrate or carbonate.

Niobium is quinquivalent, and forms only one class of compounds, namely, a chloride, NbCl_5 ; oxide, Nb_2O_5 ; oxychloride NbOCl_3 , etc.

Niobic Oxide, Nb_2O_5 , is formed when the metal burns in the air. It is prepared from columbite, etc., by fusing the levigated mineral in a platinum crucible with 6 or 8 parts of acid potassium sulphate, removing soluble salts by boiling the fused mass with water, digesting the residue with ammonium sulphide to dissolve tin and tungsten, boiling with strong hydrochloric acid to remove iron, uranium, and other metals, and finally washing with water. Niobic oxide is thus obtained generally mixed with tantalic oxide, from which it is separated by means of hydrogen and potassium fluoride, HF.KF , which converts the tantalum into sparingly soluble potassium tantalofluoride, 2KF.TaF_5 , and the niobium into easily soluble potassium nioboxyfluoride, $2\text{KF.NbOF}_3\text{.Aq.}$

Niobic oxide is also produced by decomposing niobic chloride, or oxychloride, with water; when pure it has a specific gravity of 4.4 to 4.5. It is an acid oxide, uniting with basic oxides, and forming salts called niobates, some of which occur as natural minerals: columbite, for example, being a ferro-manganous niobate. The *potassium niobates* crystallize readily, and in well-defined forms. Marignac has obtained the salts $4\text{K}_2\text{O.3Nb}_2\text{O}_5\text{.16Aq.}$ crystallizing in monoclinic prisms; $8\text{K}_2\text{O.7Nb}_2\text{O}_5\text{.32Aq.}$ in pyramidal monoclinic crystals; $3\text{K}_2\text{O.2Nb}_2\text{O}_5\text{.13Aq.}$ in rhomboidal prisms; and $\text{K}_2\text{O.3Nb}_2\text{O}_5\text{.Aq.}$ as a pulverulent precipitate, by boiling a solution of potassium nioboxyfluoride with potassium carbonate. The *sodium niobates* are crystalline powders which decompose during washing. There is also a sodium and potassium niobate, containing $\text{Na}_2\text{O.3K}_2\text{O.3Nb}_2\text{O}_5\text{.9Aq.}$

Niobic Chloride, NbCl_5 , is obtained, together with the oxychloride, by heating an intimate mixture of niobic oxide and charcoal in a stream of chlorine gas. It is yellow, volatile, and easily fusible. Its observed vapor-density, according to Deville and Troost, is 9.6 referred to air, or 138.6 referred to hydrogen as unity: by calculation for a two-volume condensation, it is $\frac{94 + 5 \times 35.5}{2} = 137.75$. The *oxychloride*, NbOCl_3 , is white, vola-

tile, but not fusible: its specific gravity, referred to hydrogen, is by observation, 114.06; by calculation, $\frac{94 + 16 + 3 \times 35.5}{2} = 109.25$. Both these compounds are converted by water into niobic oxide.

Niobic Oxyfluoride, NbOF_3 , is formed by dissolving niobic oxide in hydrofluoric acid. It unites with the fluorides of the more basic metals, forming salts isomorphous with the titanofluorides, stannofluorides, and tungstofluorides, 1 atom of oxygen in these salts taking the place of 2 atoms of fluorine. Marignac has obtained five potassium nioboxyfluorides, all perfectly crystallized, namely:—

| | |
|----------------------------------|---------------------------------------|
| $2\text{KF.NbOF}_3\text{.Aq.}$ | crystallizing in monoclinic plates, |
| 3KF.NbOF_3 | " cuboid forms (system undetermined), |
| 3KF.HF.NbOF_3 | " monoclinic needles, |
| $5\text{KF.3NbOF}_3\text{.Aq.}$ | " hexagonal prisms, |
| $4\text{KF.3NbOF}_3\text{.2Aq.}$ | " triclinic prisms. |

Potassium niobylfluoride, $3\text{KF} \cdot \text{NbF}_5$, separates in shining monoclinic needles from a solution of the first of the above-mentioned nioboxylfluorides in hydrofluoric acid. Nioboxylfluorides of ammonium, sodium, zinc, and copper have also been obtained.

The isomorphism of these salts with the stannofluorides, titanofluorides, and tungstofluorides, shows clearly that the existence of isomorphism between the corresponding compounds of any two elements, must not be taken as a decided proof that those elements are of equal atomicity: for in the case now under consideration, we have isomorphous salts formed by tin and titanium, which are tetrads, niobium, which is a pentad, and tungsten, which is a hexad.

The compounds of niobium cannot easily be mistaken for those of any other metal except tantalum. The most characteristic reactions of niobates and tantalates with liquid reagents are the following:—

| | <i>Niobates.</i> | <i>Tantalates.</i> |
|------------------------|---|--|
| Hydrochloric acid . . | White precipitate, insoluble in excess. | White precipitate, soluble in excess. |
| Ammonium chloride . | Precipitation slow and incomplete. | Complete precipitation as acid ammonium tantalate. |
| Potassium ferrocyanide | Red precipitate. | Yellow precipitate. |
| " ferricyanide | Bright yellow precipitate. | White precipitate. |
| Infusion of galls . . | Orange-red precipitate. | Light yellow precipitate. |

Niobic oxide, heated with borax in the outer blow-pipe flame, forms a colorless bead, which, if the oxide is in sufficient quantity, becomes opaque by interrupted blowing or flaming. In microcosmic salt it dissolves abundantly, forming a colorless bead in the outer flame, and in the inner a violet-colored, or if the bead is saturated with the oxide, a beautiful blue bead, the color disappearing in the outer flame.

CLASS VI.—HEXAD METALS.

CHROMIUM

Atomic weight, 52.2. Symbol, Cr.

Chromium is found in the state of oxide, in combination with iron oxide, in some abundance in the Shetland Islands, and elsewhere: as lead chromate it constitutes a very beautiful mineral, from which it was first obtained. The metal itself is prepared in a half-fused condition by mixing the oxide with half its weight of charcoal powder, inclosing the mixture in a crucible lined with charcoal, and then subjecting it to the very highest heat of a powerful furnace.

Deville has prepared metallic chromium by reducing pure chromium sesquioxide with an insufficient quantity of charcoal, in a lime crucible. Thus prepared, metallic chromium is less fusible than platinum, and as hard as corundum. It is readily acted upon by dilute hydrochloric acid, less so by dilute sulphuric acid, and not at all by concentrated nitric acid. Frémy obtained chromium in small cubic crystals, by the action of sodium vapor on chromium trichloride at a red heat. The crystalline chromium resists the action of concentrated acids, even of nitro-muriatic acid.

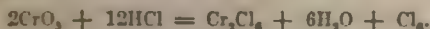
Chromium forms a hexafluoride, CrF_6 , and a corresponding oxide, CrO_6 , analogous to sulphuric oxide; also, an acid, H_2CrO_4 , analogous to sulphuric acid, with corresponding salts, the chromates, which are isomorphous with the sulphates. In its other compounds, chromium resembles iron, forming the chromic compounds, Cr_2Cl_6 , Cr_2O_3 , etc., in which it is apparently trivalent, but really quadrivalent, and the chromous compounds, CrCl_2 , CrO , etc., in which it is bivalent.

Chlorides.—The dichloride, or *Chromous chloride*, CrCl_2 , is prepared by heating the violet-colored trichloride, contained in a porcelain or glass tube, to redness in a current of perfectly dry and pure hydrogen gas: hydrochloric acid is then disengaged, and a white foliated mass is obtained, which dissolves in water with great elevation of temperature, yielding a blue solution, which, on exposure to the air, absorbs oxygen with extraordinary energy, acquiring a deep-green color, and passing into the state of chromic oxychloride, $\text{Cr}_2\text{Cl}_6 \cdot \text{Cr}_2\text{O}_3$. Chromous chloride is one of the most powerful reducing or deoxidizing agents known, precipitating calomel from a solution of mercuric chloride, instantly converting tungstic acid into blue tungsten oxide, and precipitating gold from a solution of auric chloride. It forms, with ammonia, a sky-blue precipitate, which turns green on exposure to the air; with ammonia and sal-ammoniac, a blue solution turning red on exposure to the air; and with ammonium sulphide, a black precipitate of chromous sulphide.

The trichloride, or *Chromic chloride*, Cr_2Cl_6 , is obtained in the anhydrous state by heating to redness in a porcelain tube a mixture of chromium sesquioxide and charcoal, and passing dry chlorine gas over it. The trichloride sublimes, and is deposited in the cool part of the tube, in the form of beautiful crystalline plates of a pale-violet color. It is totally insoluble in water under ordinary circumstances, even at the boiling heat. It dissolves, however, and assumes the deep-green hydrated state in water con-

ing an exceedingly minute quantity of the dichloride in solution. The action is marked by the evolution of much heat.

A green hydrated chromic chloride is easily formed by dissolving the hydrate in hydrochloric acid, or by boiling lead chromate, or chromate, or a solution of chromic acid, with hydrochloric acid and being agent, such as alcohol, or sulphurous acid, or even with hydrochloric acid alone:—



A solution thus obtained exhibits the same characters as the chromic salts. When evaporated, it leaves a dark-green syrup, which, heated to 1000° in a stream of dry air, yields a green mass containing $9\text{H}_2\text{O}$. The same solution evaporated in a vacuum yields green star crystals containing $\text{Cr}_2\text{Cl}_6 \cdot \text{H}_2\text{O}$.

Oxides.—The *trifluoride*, or *Chromic fluoride*, Cr_2F_6 , is obtained by heating the dried sesquioxide with hydrofluoric acid, and strongly heating the mass, as a dark-green substance, which melts at a high temperature, and sublimes when still more strongly heated, in shining regular prisms.

Hexafluoride, CrF_6 , is formed by distilling lead chromate with fluorinated fuming oil of vitriol in a leaden retort, and condensing the vapor in a cooled and dry leaden receiver. It then condenses to a blood-red liquid, which volatilizes when its temperature rises a few degrees higher. The vapor is red, and, when inhaled, produces violent irritation and severe oppression of the lungs. The hexafluoride is decomposed by water, yielding hydrofluoric and chromic acids. A fluoride, intermediate in composition between the two just described, is obtained in a pure form by decomposing the brown dioxide in hydrofluoric acid. The fluoride is red, and yields by evaporation a rose-colored salt, which is altered without alteration by water, and precipitated brown by ammonia.

Acids.—Chromium forms five oxides, containing CrO , Cr_2O_3 , Cr_2O_5 , CrO_2 , and CrO_3 , the first three being analogous in composition to the three of iron.

Chromous oxide, or *Chromous oxide*, CrO , is formed on adding potash to a solution of chromous chloride, as a brown precipitate, which speedily changes to deep foxy-red, with disengagement of hydrogen, being converted into a higher oxide. Chromous oxide is a powerful base, forming the salts, which absorb oxygen with extreme avidity. Potassiochromous sulphate has the composition $\text{CrK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, like the other members of the same group.

Chromic tetroxide, $(\text{CrO})_4 = \text{CrO} \cdot \text{Cr}_2\text{O}_3$, is the above-mentioned brownish precipitate produced by the action of water upon the monoxide. The decomposition is not complete without boiling. This oxide corresponds to the magnetic oxide of iron, and is not salifiable.

Chromic oxide, or *Chromic oxide*, Cr_2O_3 .—When mercurous chromate, prepared by mixing solutions of mercurous nitrate and potassium chromate, is exposed to a red heat, it is decomposed, pure chromium oxide, having a fine green color, remaining. In this state the oxide is infusible, and insoluble in acids. The anhydrous sesquioxide may be prepared in a beautifully crystalline form by heating potassiochromate, $\text{K}_2\text{O} \cdot 2\text{CrO}_3$, to full redness in an earthen crucible. One-fourth of the chromium trioxide contained in that salt then suffers decomposition, oxygen being disengaged and sesquioxide left. The melted mass

is then treated with water, which dissolves out neutral potassium mate, and the oxide is, lastly, washed and dried. Chromium sesquioxide communicates a fine green tint to glass, and is used in enamel painting. The crystalline sesquioxide is employed in the manufacture of razor-stones. From a solution of chromium sesquioxide in potash or soda, green tinuous hydrated sesquioxide of chromium is separated on standing. It is finely powdered and dried over sulphuric acid, it consists of Cr_2O_3 . A hydrate may also be prepared by boiling a somewhat dilute solution of potassium dichromate, strongly acidulated with hydrochloric acid, small successive portions of sugar or alcohol. In the former case the dioxide escapes: in the latter, aldehyde and also acetic acid are formed, and the chromic acid of the salt becomes converted into chromium hydride, the color of the liquid changing from red to deep green. The action may also be effected, as already observed, by hydrochloric acid. A slight excess of ammonia precipitates the hydrate from its solution, has a pale purplish-green color, which becomes full green on ignition; great shrinking of volume and sudden incandescence are observed, the hydrate is decomposed by heat.

Chromium sesquioxide is a weak base, resembling, and isomorphous with iron sesquioxide and alumina; its salts (chromic salts) have a green or purple color, and are said to be poisonous.

Chromic sulphate, $(\text{Cr}_2)(\text{SO}_4)_3$, is prepared by dissolving the hydrate in dilute sulphuric acid. It unites with the sulphates of potash and ammonium, giving rise to magnificent double salts, which crystallize in regular octahedrons of a deep claret-color, and possess a constitution resembling that of common alum, the aluminium being replaced by chromium. The ammonium-salt, for example, has the composition $(\text{Cr}^{+++})_2(\text{SO}_4)_7 \cdot 12\text{Aq}$. The finest crystals are obtained by spontaneous evaporation; the solution being apt to be decomposed by heat.

The *dioxide*, CrO_2 , which is, perhaps, a chromic chromate, $\text{CrO}_3 \cdot \text{CrO}_2$, a brown substance obtained by digesting chromic oxide with excess of chromic acid, or by partial reduction of chromic acid with alcohol, sulphuric acid, etc.

Chromium Trioxide, CrO_3 ; in combination with water, forming *chromic acid*, $\text{CrO}_3 \cdot \text{H}_2\text{O} = \text{H}_2\text{CrO}_4 = (\text{CrO}_2)^{++}(\text{OH})_2$. Whenever chromium sesquioxide is strongly heated with an alkali, in contact with air, oxygen is absorbed and the trioxide generated. Chromium trioxide may be obtained nearly pure, and in a state of great beauty, by mixing 100 measures of cold saturated solution of potassium dichromate with 150 measures of vitriol, leaving the whole to cool, pouring off the mother-liquor, leaving the crystals to drain upon a tile, closely covered by a glass jar. It is also formed by decomposing the hexafluoride with a small quantity of water. Chromium trioxide crystallizes in brilliant crimson prisms very deliquescent and soluble in water: the solution is immediately reduced by contact with organic matter.

Chromic acid is bibasic and analogous in composition to sulphuric acid; its salts are isomorphous with the corresponding sulphates.

Potassium chromate, K_2CrO_4 or $(\text{CrO}_2)^{++}(\text{OK})_2$.—This salt is made directly from the native *chrome-iron ore*, which is a compound of chromium sesquioxide and ferrous oxide, analogous to magnetic iron ore, by calcining with nitre or with potassium carbonate, or with caustic potash, the product being reduced to powder and heated for a long time with the alkali in a reverberatory furnace. The product, when treated with water, yields a yellow solution, which, by evaporation, deposits anhydrous crystals of the same color, isomorphous with potassium sulphate. Potassium chromate

has a cool, bitter, and disagreeable taste, and dissolves in 2 parts of water at 15.50°.

Potassium dichromate, or *anhydrochromate*, $K_2O \cdot 2CrO_3$ or $K_2CrO_4 \cdot CrO_3$.—When sulphuric acid is added to the preceding salt in moderate quantity, one-half of the base is removed, and the neutral chromate converted into dichromate. This salt, of which immense quantities are manufactured for use in the arts, crystallizes by slow evaporation in beautiful red tabular crystals, derived from a triclinic prism. It melts when heated, and is soluble in 10 parts of water; the solution has an acid reaction.

Potassium trichromate, $K_2O \cdot 3CrO_3$ or $K_2CrO_4 \cdot 2CrO_3$, may be obtained in crystals by dissolving the dichromate in an aqueous solution of chromic acid, and leaving it to evaporate over sulphuric acid.

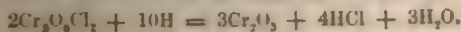
Lead chromate, $PbCrO_4$.—This salt, the *chrome-yellow* of the painter, is obtained, as a brilliant yellow precipitate, on mixing solutions of potassium chromate or dichromate with lead nitrate or acetate. On boiling it with lime-water, one-half of the acid is withdrawn, and a basic lead chromate of an orange-red color left. The basic chromate is also formed by adding lead chromate to fused nitre, and afterwards dissolving out the soluble salts by water: the product is crystalline, and rivals vermilion in beauty of tint. The yellow and orange chrome colors are fixed upon cloth by alternate application of the two solutions, and in the latter case by passing the dyed stuff through a bath of boiling lime-water.

Silver chromate, Ag_2CrO_4 .—This salt is precipitated as a reddish-brown powder when solutions of potassium chromate and silver nitrate are mixed. It dissolves in hot dilute nitric acid, and separates, on cooling, in small ruby-red platy crystals. The chromates of barium, zinc, and mercury are insoluble; the first two are yellow, the last is brick-red.

Perchromic Acid is obtained, according to Barreswil, by mixing chromic acid with dilute hydrogen dioxide, or potassium dichromate with a dilute but very acid solution of barium dioxide in hydrochloric acid; a liquid is then formed of a blue color, which is removed from the aqueous solution by ether. This very unstable compound has perhaps the composition $H_2Cr_2O_5$, or $Cr_2O_7 \cdot H_2O$, analogous to that of permanganic acid.

Chromium Dioxychloride, or *Chromyl chloride*, CrO_2Cl_2 , commonly called *Chlorochromic acid*.—When 3 parts of potassium dichromate and 3 parts of common salt are intimately mixed and introduced into a small glass retort, 9 parts of oil of vitriol then added, and heat applied as long as dense red vapors arise, this compound passes over as a heavy deep-red liquid resembling bromine: it is decomposed by water, with production of chromic and hydrochloric acids. It is analogous to the so-called chloromolybdic, chlorotungstic, and chlorosulphuric acids, in composition, and to the products which it yields when decomposed. It may be regarded as formed from the trioxide by substitution of Cl_2 for O, or from chromic acid $(CrO_3)(OH)_3$, by substitution of Cl_2 for $(OH)_3$; also as a compound of chromium hexachloride (not known in the separate state), with chromium trioxide: $CrCl_6 \cdot 2CrO_3 = 3CrO_2Cl_2$.

Trichromyl chloride, $(CrO_2)_3Cl_2$ or $CrO_2Cl - CrO_2 - CrO_2Cl$, is formed by heating the preceding compound to 180°–190° in a sealed tube: $3CrO_2Cl_2 = (CrO_2)_3Cl_2 + Cl_2$. It is a black non-crystalline powder, which deliquesces rapidly in the air to a dark reddish-brown syrupy liquid smelling of free chlorine. When gently heated in hydrogen gas it takes fire, and is resolved into chromium sesquioxide, hydrochloric acid, and water:



Reactions of Chromium compounds.—A solution of chromic chloride, or a chromic oxygen salt, is not precipitated or changed in any way by hydrogen sulphide. Ammonium sulphide throws down a grayish-green precipitate of chromic hydrate. Caustic fixed alkalis also precipitate the hydrated oxide, and dissolve it easily when added in excess. Ammonia, the same, but nearly insoluble. The carbonates of potassium, sodium, and ammonium also throw down a green precipitate of hydrate, slightly soluble in a large excess.

Chromous salts are but rarely met with; for their reactions, see Chromium dichloride, p. 408.

Chromic acid and its salts are easily recognized in solution by forming a pale yellow precipitate with barium salts, bright yellow with lead salts, brick-red with mercurous salts, and crimson with silver salts; also by their capability of yielding the green sesquioxide by reduction.

All chromium compounds, ignited with a mixture of nitre and an alkaline carbonate, yield an alkaline chromate, which may be dissolved out by water, and on being neutralized with acetic acid, will give the reactions just mentioned.

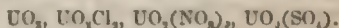
The oxides of chromium and their salts, fused with borax in either blowpipe flame, yield an emerald-green glass. The same character is exhibited by those salts of chromic acid whose bases do not of themselves impart a decided color to the bead. The production of the green color in both flames distinguishes chromium from uranium and vanadium, which give green beads in the inner flame only.

URANIUM.

Atomic weight, 240. Symbol, U.

This metal is found in a few minerals, as *pitchblende*, which is an oxide, and *uranite*, which is a phosphate; the former is its principal ore. The metal itself is isolated by decomposing the chloride with potassium or sodium, and is obtained as a black coherent powder, or in fused white malleable globules, according to the manner in which the process is conducted. It is permanent in the air at ordinary temperatures, and does not decompose water; but in the pulverulent state it takes fire at 207°C . (404.6°F .), burning with great splendor and forming a dark-green oxide. It unites also very violently with chlorine and with sulphur.

Uranium forms two classes of compounds: viz., the uranous compounds, in which it is quadrivalent, e.g., UCl_4 , UO_2 , $\text{U}(\text{SO}_4)_2$, etc., and the uranic compounds, in which it is sexvalent, e.g.,



There are also two oxides intermediate between uranous and uranic oxide. There is no chloride, bromide, iodide, or fluoride corresponding with uranic oxide, such as UCl_6 ; neither are there any normal uranic oxy-salts, such as $\text{U}(\text{NO}_3)_6$, $\text{U}(\text{SO}_4)_3$, etc.; but all the uranic salts contain the group UO_2 , which may be regarded as a bivalent radical (uranyl), uniting with acids in the usual proportions, and forming normal salts; thus—

| | | |
|---------------------------------------|-------|--------------------------------|
| Uranic oxide or Uranyl oxide | • • • | $(\text{UO}_2)\text{O}$ |
| Uranic oxychloride or Uranyl chloride | • • • | $(\text{UO}_2)\text{Cl}_2$ |
| Uranic nitrate or Uranyl nitrate | • • • | $(\text{UO}_2)(\text{NO}_3)_2$ |
| Uranic sulphate or Uranyl sulphate | • • • | $(\text{UO}_2)(\text{SO}_4)$ |

This view of the composition of the uranic salt is not, however, essential, since they may also be formulated as basic salts in the manner above illustrated.

Chlorides.—*Uranous chloride*, UCl_4 , is formed, with vivid incandescence, by burning metallic uranium in chlorine gas, also by igniting uranous oxide in hydrochloric acid gas. It crystallizes in dark-green regular octahedrons, and dissolves easily in water, forming an emerald-green solution, which is decomposed when dropped into boiling water, giving off hydrochloric acid, and yielding a brown precipitate of hydrated uranous oxide. It is a powerful deoxidizing agent, reducing gold and silver, converting ferric salts into ferrous salts, etc.

Uranic oxychloride, or *Uranyl chloride*, UO_2Cl_2 , is formed when dry chlorine gas is passed over red-hot uranous oxide, as an orange-yellow vapor, which solidifies to yellow crystalline fusible mass, easily soluble in water. It forms double salts with the chlorides of the alkali-metals,—the potassium salt, for example, having the composition, $\text{UO}_2\text{Cl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$.

Oxides.—*Uranous oxide*, UO_2 , formerly mistaken for metallic uranium, is obtained by heating the oxide, U_3O_8 , or uranic oxalate, in a current of hydrogen. It is a brown powder, sometimes highly crystalline. In the finely divided state it is pyrophoric. It dissolves in acids, forming green salts.

Uranoso-uranic oxide, $\text{U}_3\text{O}_8 = \text{UO}_2 \cdot 2\text{UO}_3$.—This oxide forms the chief constituent of pitchblende. It is obtained artificially by igniting the metal or uranous oxide in contact with the air, or by gentle ignition of uranic oxide or uranic nitrate. It forms a dark-green velvety powder, of specific gravity 7.1 to 7.3. When ignited in hydrogen, or with sodium, charcoal, or sulphur, it is reduced to uranous oxide. When ignited alone, it yields a black oxide, U_2O_3 . Uranoso-uranic oxide dissolves in strong sulphuric or hydrochloric acid, yielding a mixture of uranous and uranic salt; by nitric acid it is oxidized to uranic nitrate.

Uranic oxide, or *Uranyl oxide*, UO_3 .—Uranium and its lower oxides dissolve in nitric acid, forming uranic nitrate; and when this salt is heated in a glass tube till it begins to decompose, at 250° , pure uranic oxide remains in the form of a ochreous-yellow powder. Uranic hydrate, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, cannot be prepared by precipitating a uranic salt with alkalis, inasmuch as the precipitate always carries down alkali with it; but it may be obtained by evaporating a solution of uranic nitrate in absolute alcohol at a moderate heat, till, at a certain degree of concentration, nitrous ether, aldehyde, and other vapors are given off, and a spongy yellow mass remains, which is the hydrate. In a vacuum at ordinary temperatures, or at 100° in the air, it gives off half its water, leaving the monohydrate, $\text{UO}_3 \cdot \text{H}_2\text{O}$. This hydrate cannot be deprived of all its water without exposing it to a heat sufficient to drive off part of the oxygen, and reduce it to uranoso-uranic oxide.

Uranic oxide and its hydrates dissolve in acids, forming the uranic salts. The *nitrate*, $(\text{UO}_3)_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, may be prepared from pitchblende by dissolving the pulverized mineral in nitric acid, evaporating to dryness, adding water and filtering; the liquid yields, by due evaporation, crystals of uranic nitrate, which are purified by a repetition of the process, and, lastly, dissolved in ether. This latter solution yields the pure nitrate.

Uranates.—Uranic oxide unites with the more basic metallic oxides. The *uranates* of the alkali-metals are obtained by precipitating a uranic salt with a caustic alkali: those of the earth-metals and heavy metals, by precipitating a mixture of a uranic salt and a salt of the other metal with

ammonia, or by igniting a double carbonate or acetate of uranium and the other metal (calcio-uranic acetate, for example) in contact with the air. The uranates have, for the most part, the composition $M_2O \cdot 2UO_3$. They are yellow, insoluble in water, soluble in acids. Those which contain fixed bases are not decomposed at a red heat; but at a white heat, the uranic oxide is reduced to uranoso-uranic oxide, or by ignition in hydrogen to uranous oxide: the mass obtained by this last method easily takes fire in contact with the air. *Sodium uranate*, $Na_2O \cdot 2UO_3$, is much used for imparting a yellowish or greenish color to glass, and as a yellow pigment on the glazing of porcelain. The "uranium-yellow" for these purposes is prepared on the large scale by roasting pitchblende with lime in a reverberatory furnace; treating the resulting calcium uranate with dilute sulphuric acid; mixing the solution of uranic sulphate thus obtained with sodium carbonate, by which the uranium is first precipitated together with other metals, but then redissolved, tolerably free from impurity, by excess of the alkali; and treating the liquid with dilute sulphuric acid, which throws down hydrated sodium uranate, $Na_2O \cdot 2UO_3 \cdot 6Aq$. *Ammonium uranate* is but slightly soluble in pure water, and quite insoluble in water containing sal-ammoniac; it may, therefore, be prepared by precipitating a solution of sodium-uranate with that salt. It occurs in commerce as a fine deep yellow pigment, also called "uranium yellow." This salt, when heated to redness, leaves pure uranoso-uranic oxide, and may, therefore, serve as the raw material for the preparation of other uranium compounds.

Uranous salts form green solutions, from which *caustic alkalis* throw down a red-brown gelatinous precipitate of uranous hydrate; *alkaline carbonates*, green precipitates, which dissolve in excess, especially of ammonium carbonate, forming green solutions. *Ammonium sulphide* forms a black precipitate of uranous sulphide; *hydrogen sulphide*, no precipitate.

Uranic salts are yellow, and yield with *caustic alkalis* a yellow precipitate of alkaline uranate, insoluble in excess of the reagent. *Alkaline carbonates* form a yellow precipitate, consisting of a carbonate of uranium and the alkali-metal, soluble in excess, especially of acid ammonium or potassium carbonate. *Ammonium sulphide* forms a black precipitate of uranic sulphide. *Hydrogen sulphide* forms no precipitate, but reduces the uranic to a green uranous salt. *Potassium ferrocyanide* forms a red-brown precipitate.

All uranium compounds, fused with *phosphorus salt* or *borax* in the outer blowpipe flame, produce a clear yellow glass, which becomes greenish on cooling. In the inner flame the glass assumes a green color, becoming still greener on cooling. The oxides of uranium are not reduced to the metallic state by fusion with sodium carbonate on charcoal.

Uranium compounds are used, as already observed, in enamel painting and for the staining of glass, uranous oxide giving a fine black color, and uranic oxide a delicate greenish-yellow, highly fluorescent glass. Uranium salts are also used in photography.

TUNGSTEN or WOLFRAM.

Atomic weight, 184. Symbol, W.

TUNGSTEN is found, as ferrous tungstate, in the mineral *wolfram*, tolerably abundant in Cornwall; occasionally also as calcium tungstate (*scheelite* or *tungsten*), and as lead tungstate (*scheelite*). Metallic tungsten is obtained

in the state of a dark-gray powder, by strongly heating tungstic oxide in a stream of hydrogen, but requires for fusion an exceedingly high temperature. It is a white metal, very hard and brittle: it has a density of 17.4. Heated to redness in the air, it takes fire and reproduces tungstic oxide.

Tungsten forms two classes of compounds, in which it is quadrivalent and sexvalent respectively, and a third class, of intermediate composition, in which it is apparently quinquivalent.

Chlorides.—These compounds are formed by heating metallic tungsten in chlorine gas. The *hexchloride*, or *tungstic chloride*, WCl_6 , is also produced, together with oxychloride, by the action of chlorine on an ignited mixture of tungstic oxide and charcoal. The oxychlorides, being more volatile than the hexchloride, may be separated from it by sublimation. The hexchloride forms dark violet scales or fused crusts, having a bluish-black metallic iridescence. By contact with water or moist air, it is converted into hydrochloric and tungstic acids. The chlorides, WCl_6 , WCl_4 , and WCl_3 , are formed when the hexchloride is heated in hydrogen gas. The two former are crystalline: the dichloride is a loose gray powder, destitute of crystalline structure.*

A pentabromide and hexbromide are formed by the action of bromine in excess on tungsten.—The *hexfluoride*, WF_6 , is obtained by evaporating a solution of tungstic acid in hydrofluoric acid.

Oxides.—Tungsten forms three oxides, WO_2 , WO_3 , and W_2O_5 , neither of which exhibits basic properties, so that there are no tungsten salts in which the metal replaces the hydrogen of an acid, or takes the electropositive part. The trioxide exhibits decided acid tendencies, uniting with basic metallic oxides, and forming crystallizable salts called *tungstates*. The pentoxide may be regarded as a compound of the other two.

The *dioxide*, or *Tungstous oxide*, WO_2 , is most easily prepared by exposing tungstic oxide to hydrogen, at a temperature not exceeding dull redness. It is a brown powder, sometimes assuming a crystalline appearance and an imperfect metallic lustre. It takes fire when heated in the air, and burns, like the metal itself, to tungstic oxide. It forms a definite compound with soda.

The *trioxide*, or *Tungstic oxide*, WO_3 , is most easily prepared from native calcium tungstate by digestion in nitric or hydrochloric acid, the soluble calcium salt thereby produced being washed out with water, and the remaining tungstic acid ignited. From wolfram it may be prepared by repeatedly digesting the mineral in strong hydrochloric acid, ultimately with addition of a little nitric acid, to dissolve out the iron and manganese; dissolving the remaining tungstic acid in aqueous ammonia; evaporating to dryness; and heating the residual ammonium tungstate in contact with the air. Tungstic oxide is a yellow powder insoluble in water, and in most acids, but soluble in alkalis. The hot solutions of the resulting alkaline tungstates, when neutralized with an acid, yield a yellow precipitate of *anhydrous monohydrate* or *tungstic acid*, H_2WO_4 or $H_2O.WO_3$. Cold dilute solutions, on the other hand, yield with acids a white precipitate, consisting of *tungstic dihydrate*, or *hydrated tungstic acid*, $2H_2O.WO_3$, or $H_2WO_4.H_2O$. Tungstic acid reddens litmus and dissolves easily in alkalis.

Tungstates.—Tungstic acid unites with bases in various and often in very unusual proportions. It is capable of existing also in two isomeric modifications, viz.—1. *Ordinary tungstic acid*, which is insoluble in water,

* Roscoe, Journal of the Chemical Society, 1872, p. 287.

and forms insoluble salts with all metals, except the alkali-metals and magnesium; 2. *Metatungstic acid*, which is soluble in water, and forms soluble salts with nearly all metals. Ordinary tungstic acid forms normal salts containing M_2WO_6 or $M_2O.WO_3$, and acid salts containing $3M_2O.7WO_3$, which may perhaps be regarded as double salts composed of diacid and triacid tungstates, that is, as $2(M_2O.2WO_3) + M_2O.3WO_3$. The tungstates of potassium and sodium, especially the latter, are sometimes used as mordants in dyeing, in place of stannates; also for rendering muslin and other light fabrics unflammable. Tungstous tungstate, $WO_2.WO_3$, which has the composition of *tungsten pentoxide*, W_2O_5 , is a blue substance formed by reducing tungstic oxide or tungstic acid with zinc and hydrochloric acid; also by heating ammonium tungstate to redness in a retort.

Metatungstates.—These salts, which have the composition of quadric acid tungstates, $M_2O.4WO_3$, are formed from ordinary tungstates by addition of tungstic acid, or by removing part of the base by means of an acid. They are for the most part soluble and crystallizable. By decomposing barium metatungstate with dilute sulphuric acid, and evaporating the filtrate in a vacuum, hydrated metatungstic acid is obtained in quadric octohedrous apparently containing $H_2O.4WO_3 + 31Aq.$; it is very soluble in water.

Silicotungstates.*—By boiling gelatinous silica with acid potassium tungstate, a crystalline salt is obtained, having the composition of a diacid potassium tungstate, $6(K_2O.2WO_3)$, or $K_{12}O_6.12WO_3$, in which one-third of the potassium is replaced by silicon, viz., $K_8Si^bO_6.12WO_3$, so that the silicon here enters as a *basylous* element. The resulting solution yields with mercurous nitrate a precipitate of *mercurous silicotungstate*: this, when decomposed by an equivalent quantity of hydrochloric acid, yields a solution of *hydrogen silicotungstate*, or *silicotungstic acid*; and the other silicotungstates, which are all soluble, are obtained by treating the acid with carbonates.

Silicodectitungstic acid, $H_8Si^bO_6.10WO_3$, is obtained as an ammonium salt by boiling gelatinous silica with solution of acid ammonium tungstate; and from this, the acid and its other salts may be obtained in the same manner as the preceding. The silicodectitungstates are very unstable, and the acid is decomposed by mere evaporation, depositing silica, and being converted into *tungstosilicic acid*, which is isomeric with silicotungstic acid, and likewise decomposes carbonates. All three of these acids are capable of exchanging either one-half or the whole of their basic hydrogen for metals, thereby forming acid and neutral salts; silicotungstic acid also forms an acid sodium salt in which only one-fourth of the hydrogen is replaced by sodium.

Tungsten Sulphides.—The *disulphide*, or *Tungstous sulphide*, WS_2 , is obtained in soft, black, needle-shaped crystals by igniting tungsten, or one of its oxides, with sulphur.

The *trisulphide*, or *Tungstic sulphide*, WS_3 , is formed by dissolving tungstic acid in ammonium sulphide, and precipitating with an acid, or by adding hydrochloric acid to the solution of an alkaline tungstate saturated with hydrogen sulphide. It is a light-brown precipitate, turning black when dry. It unites easily with basic metallic sulphides, forming the *sulphur-tungstates*, M_2WS_4 , analogous to the normal tungstates.

Reactions of Tungsten compounds.—Soluble tungstates, or metatungstates, supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic

* Maignac, Ann. Chim. Phys. [4] iii. 5; Watts's Dictionary of Chemistry, v. 615.

acid, yield, on the introduction of a piece of zinc, a beautiful blue color, arising from the formation of blue tungsten oxide. A soluble tungstate, mixed with *ammonium sulphide*, and then with excess of acid, yields a light-brown precipitate of tungstic sulphide, soluble in ammonium sulphide. *Hydrogen sulphide* does not precipitate the acidulated solution of a tungstate, but turns it blue, owing to the formation of the blue oxide. Ordinary tungstates give, with *potassium ferrocyanide*, after addition of hydrochloric acid, a brown flocculent precipitate, soluble in pure water free from acid; metatungstates give no precipitate. *Acids*, added to solutions of ordinary tungstates, throw down a white or yellow precipitate of tungstic acid; with metatungstates no precipitate is obtained.

All tungsten compounds form colorless beads with borax and phosphorus salt, in the outer blowpipe flame. With borax, in the inner flame, they form a yellow glass, if the quantity of tungsten is somewhat considerable, but colorless with a smaller quantity. With phosphorus salt in the inner flame they form a glass of a pure blue color, unless metallic oxides are present, which modify it; in presence of iron the glass is blood-red, but the addition of metallic tin renders it blue.

Steel, alloyed with a small quantity of tungsten, acquires extraordinary hardness. Wootz, or Indian steel, contains tungsten. Tungsten has also a remarkable effect on steel in increasing its power of retaining magnetism when hardened. A horse-shoe magnet of ordinary steel, weighing two pounds, is considered of good quality when it bears seven times its own weight; but, according to Siemens, a similar magnet made with steel containing tungsten may be made to carry twenty times its weight suspended from the armature.*

MOLYBDENUM.

Atomic weight, 96. Symbol, Mo.

This metal occurs in small quantity as sulphide, or *molybdenite*, and as lead molybdate, or *wulfenite*. Metallic molybdenum is obtained by exposing molybdic oxide in a charcoal-lined crucible to the most intense heat that can be obtained. It is a white, brittle, and exceedingly infusible metal, having a density of 8.6, and oxidizing, when heated in the air, to molybdic oxide.

Chlorides.—Molybdenum forms four chlorides, containing MoCl_2 , MoCl_3 , or Mo_2Cl_4 , MoCl_4 , and MoCl_5 , or $\text{Mo}_2\text{Cl}_{10}$.

The pentachloride is produced when metallic molybdenum (previously freed from oxide by ignition in hydrogen chloride) is heated for some time in a stream of dry chlorine gas.

The pentachloride, heated to about 250° in a stream of hydrogen, is reduced to the red, difficultly volatile trichloride, MoCl_3 , or Mo_2Cl_6 ; and this compound, heated to redness in an atmosphere of carbon dioxide free from oxygen, is resolved, according to the equation $\text{Mo}_2\text{Cl}_6 = \text{MoCl}_2 + \text{MoCl}_4$, into the yellow dichloride, which remains in the tube, and the brown tetrachloride, which sublimates or is carried forward by the stream of gas.

Of these four chlorides the pentachloride is the only one which crys-

* Journal of the Chemical Society, July, 1868. 2d Series, vol. vi. p. 284.

tallizes distinctly, and melts and volatilizes without decomposition. The pure pentachloride is black. Its vapor has a dark brown-red color. The sulphur-yellow dichloride, and the red trichloride, which is deceptively like amorphous phosphorus, have been obtained only in the amorphous state; the tetrachloride is an indistinctly crystalline brown sublimate. In an atmosphere of carbon dioxide, the dichloride bears a bright red heat without melting or volatilizing; the trichloride, under the same circumstances, is resolved into di- and tetrachloride, which, when again heated, splits up into pentachloride which sublimes, and trichloride which remains behind.

The di- and trichloride are quite permanent in the air at ordinary temperatures, and insoluble in water; the tetra- and pentachloride, on the other hand, are extremely susceptible of the action of oxygen, and more particularly of moisture.

The dichloride is insoluble in *nitric acid*, which, however, dissolves all the other chlorides. The dichloride dissolves easily in hot *hydrochloric acid*, with aid of heat, and crystallizes therefrom on cooling, in long, shining, yellow needles, $\text{Mo}_2\text{Cl}_4 \cdot 3\text{H}_2\text{O}$, which give off $2\text{H}_2\text{O}$ at 100° .*

The *bromides* of molybdenum correspond in composition with the chlorides; there is also an oxybromide containing $\text{Mo}^{\text{VI}}\text{Br}_2\text{O}_3$.

Fluorides.—Molybdenum forms three fluorides, MoF_3 , MoF_4 , and MoF_5 , which are obtained by dissolving the corresponding oxides in hydrofluoric acid. The *hexfluoride* is not known in the free state, but only in combination with basic metallic fluorides and molybdates; thus there is a potassium salt containing $\text{K}_2\text{MoO}_4 \cdot \text{K}_2\text{MoF}_6$.

Oxides.—Molybdenum forms the three oxides, MoO , MoO_2 , and MoO_3 , besides several oxides intermediate between the last two, which may be regarded as molybdic molybdates.

The *monoxide*, or *Molybdous oxide*, MoO , is produced by bringing the dioxide or trioxide, in presence of one of the stronger acids, in contact with any of the metals which decompose water. Thus, when zinc is immersed in a concentrated solution of an alkaline molybdate mixed with a quantity of hydrochloric acid sufficient to redissolve the precipitate first thrown down, zinc chloride and molybdous chloride are formed. The dark-colored solution thus obtained is mixed with a large quantity of caustic potash, which precipitates a black hydrated molybdous oxide, and retains the zinc oxide in solution. The freshly-precipitated hydrate is soluble in acids and ammonium carbonate; when heated in the air, it burns to dioxide, but when dried in a vacuum, it leaves the black anhydrous monoxide.

The *dioxide*, or *Molybdic oxide*, MoO_2 , is obtained in the anhydrous state by heating sodium molybdate with sal-ammoniac, the molybdic trioxide being reduced to dioxide by the hydrogen of the ammoniacal salt; or, in the hydrated state, by digesting metallic copper in a solution of molybdic acid in hydrochloric acid, until the liquid assumes a red color, and then adding a large excess of ammonia. The anhydrous dioxide is deep brown and insoluble in acids; the hydrate resembles ferric hydrate, and dissolves in acids, yielding red solutions. It is converted into molybdic acid by strong nitric acid.

Trioxide, MoO_3 .—To obtain this oxide (commonly called *Molybdic acid*), native molybdenum sulphide is roasted, at a red heat, in an open vessel, and the impure molybdic trioxide thence resulting is dissolved by ammonia. The filtered solution is evaporated to dryness, and the salt is taken up by water and purified by crystallization. It is, lastly, decomposed by

* Liechti and Kempt, Liebigs Annalen, c. lxx. 344.

heat, and the ammonia expelled. The trioxide may also be prepared by decomposing native lead molybdate with sulphuric acid. It is a white crystalline powder, fusible at a red heat, and slightly soluble in water. The solution contains *molybdic acid*, but this acid, or hydrate, is not known in the solid state. The trioxide is easily dissolved by alkalies, and forms two series of salts, viz., *normal or neutral molybdates*, R_2MoO_4 , or $R_2O.MoO_3$, and *anhydromolybdates*, or *lunomolybdates*, $R_2MoO_4.MoO_3$, or $R_2O.2MoO_3$, the symbol R denoting a univalent metal. The neutral molybdates of the alkali-metals are easily soluble in water, and their solutions yield, with the stronger acids, a precipitate, either of a less soluble bimolybdate, or of the anhydrous trioxide. The other molybdates are insoluble, and are obtained by precipitation. *Lead Molybdate*, $PbMoO_4$, occurs native in yellow quadratic plates and octohedrons.

Sulphides.—Molybdenum forms three sulphides, MoS_2 , MoS_3 , and MoS_4 , the last two of which are acid sulphides, forming sulphur-salts. The *disulphide*, or *Molybdic sulphide*, MoS_2 , occurs native, as *molybdenite*, in crystalline-laminar masses, or tabular crystals, having a strong metallic lustre and lead-gray color, and forming a gray streak on paper, like plumbago. The same compound is produced artificially by heating either of the higher sulphides, or by igniting the trioxide with sulphur. When roasted in contact with the air, it is converted into trioxide.

The *trisulphide*, MoS_3 , commonly called *Sulphomolybdic acid*, is obtained by passing hydrogen sulphide into a concentrated solution of an alkaline molybdate, and precipitating with an acid. It is a black-brown powder, which is dissolved slowly by alkalies, more easily by alkaline sulphides and sulphhydrates, forming sulphur salts called *Sulphomolybdates*. Most of these salts have the composition R_2MoS_4 , or $R_2S.MoS_3$, analogous to that of the molybdates. The sulpho-molybdates of the alkali-metals, alkaline earth-metals, and magnesium, are soluble in water, forming solutions of a fine red color; the rest are insoluble.

Tetrasulphide, MoS_4 .—This is also an acid sulphide, forming salts called *peroxsulphomolybdates*, the general formula of which is R_2MoS_5 , or $R_2S.MoS_4$. The *potassium salt* is obtained by boiling the sulphomolybdate with molybdenum trisulphide.

Molybdous salts, obtained by dissolving molybdous oxide in acids, are opaque and almost black. They yield, with *hydrogen sulphide*, a brown-black precipitate soluble in ammonium sulphide; with *alkalies*, and *alkaline carbonates*, a brownish-black precipitate of molybdous hydrate, easily soluble in acid potassium carbonate, or in ammonium carbonate; with *potassium ferrocyanide*, a dark brown precipitate; with *sodium phosphate*, a white precipitate.

Solutions of molybdic salts have a reddish-brown color. When heated in the air, they have a tendency to become blue by oxidation. In contact with metallic zinc, they first blacken and then yield a black precipitate of molybdous hydrate. Their reactions with *alkalies*, *hydrogen sulphide*, etc., are similar to those of molybdous salts; but the precipitates are lighter in color.

Molybdates are colorless unless they contain a colored base. Solutions of the alkaline molybdates yield with *acids* a precipitate of molybdic trioxide, soluble in excess of the precipitant. They are colored yellow by *hydrogen sulphide*, from formation of a sulpho-molybdate of the alkali-metal, and then yield with acids a brown precipitate of molybdenum trisulphide. This is an extremely delicate test for molybdic acid. They form white precipitates with the salts of the *earth-metals*, and precipitates of various colors with salts of the *heavy metals*. When *ortho-phosphoric acid*, or a liquid

containing it, is added to the solution of ammonium molybdate, together with an excess of hydrochloric acid, the liquid turns yellow, and after a while deposits a yellow precipitate of molybdic trioxide, combined with small quantities of phosphoric acid and ammonia. This precipitate is soluble in ammonia and likewise in excess of the phosphate. The reaction is therefore especially adapted for the detection of small quantities of phosphoric acid. The pyrophosphates and metaphosphates do not produce the yellow precipitate. *Arsenic acid* gives a similar reaction.

All the oxides of molybdenum form, with *borax*, in the outer blow-pipe flame, a bead which is yellow while hot, and colorless on cooling; in the inner flame, a dark brown bead, which is opaque if excess of molybdenum is present. By long continued heating, the molybdic oxide may be separated in dark brown flakes, floating in the clear yellow glass. With *phosphorus salt* in the outer flame, all oxides of molybdenum give a bead which is greenish while hot, and colorless on cooling; in the inner flame a clear green bead, from which molybdic oxide cannot be separated by continued heating.

CLASS VII.—HEPTAD METALS.

MANGANESE, as already observed, is the only known metal referable to this class, and it is more conveniently described in connection with the iron metals.

CLASS VIII.—GROUP I.—IRON METALS.

IRON.

Atomic weight, 56. Symbol, Fe (Ferrum).

This is the most important of all the metals: there are few substances to which it yields in interest, when it is considered how very intimately the knowledge of its properties and uses is connected with human civilization.

Metallic iron is of exceedingly rare occurrence: it has been found at Canaan, in Connecticut, forming a vein about two inches thick in mica-slate, but it enters into the composition of many of these extraordinary stones known to fall from the air, called *meteorites*. Isolated masses of soft malleable iron also, of large dimensions, lie loose upon the surface of the earth in South America and elsewhere, and are presumed to have had a similar origin: these latter, in common with the iron of the undoubted meteorites, contain nickel. In an oxidized condition, the presence of iron may be said to be universal: it constitutes a great part of the common coloring matter of rocks and soils; it is contained in plants, and forms an essential component of the blood of the animal body. It is also very common in the state of bisulphide. Pure iron may be prepared, according to Mitscherlich, by introducing into a Hessian crucible 4 parts of fine iron wire cut small, and 1 part of black iron oxide. This is covered with a mixture of white sand, lime, and potassium carbonate, in the proportions used for glass-making, and a cover being closely applied, the crucible is exposed to a very high degree of heat. A button of pure metal is then obtained, the traces of carbon and silicon present in the wire having been removed by the oxygen of the oxide.

Pure iron has a white color and perfect lustre: it is extremely soft and tough, and has a specific gravity of 7.8. Its crystalline form is probably the cause, to judge from appearances occasionally exhibited. In good bar-iron or wire, a distinct fibrous texture may always be observed when the metal has been attacked by rusting or by the application of an acid, and upon the perfection of this fibre much of its strength and value depends. Iron is the most tenacious of all the metals, a wire $\frac{1}{8}$ of an inch in diameter bearing a weight of 60 lbs. It is very difficult of fusion, and before becoming liquid passes through a soft or pasty condition. Pieces of iron, pressed or hammered together in this state, cohere into a single mass: the operation is termed *welding*, and is usually performed by sprinkling a little sand over the heated metal, which combines with the superficial film of oxide, forming a fusible silicate, which is subsequently forced out from between the pieces of iron by the pressure applied: clean surfaces of metal are thus presented to each other, and union takes place without difficulty.

Iron does not oxidize in dry air at common temperatures: heated to redness, it becomes covered with a scaly coating of black oxide, and at a high white heat burns brilliantly, producing the same substance. In oxygen gas the combustion occurs with still greater ease. The finely divided spongy metal, prepared by reducing the red oxide with hydrogen gas, takes fire spontaneously in the air. Pure water, free from air and carbonic

acid, does not tarnish a surface of polished iron, but the combined agency of free oxygen and moisture speedily leads to the production of rust, which is a hydrate of the sesquioxide. The rusting of iron is wonderfully promoted by the presence of a little acid vapor. At a red heat, iron decomposes water, evolving hydrogen, and passing into the black oxide. Dilute sulphuric and hydrochloric acids dissolve it freely, with separation of hydrogen. Iron is strongly magnetic up to a red heat, when it loses all traces of that remarkable property.

Iron forms two classes of compounds; namely the ferrous compounds, in which it is bivalent, *e. g.*, FeCl_2 , FeO , FeSO_4 , etc., and the ferric compounds, in which it may be regarded either as trivalent like aluminium, or as quadrivalent: ferric chloride, for example, may be either FeCl_3 or $\text{Fe}_2\text{Cl}_6 = \text{Cl}_3\text{Fe}-\text{FeCl}_3$; the vapor-density of this compound, as determined by Deville, is in favor of the latter formula.

Chlorides.—The dichloride, or *Ferrous chloride*, FeCl_2 , is formed by transmitting dry hydrochloric acid gas over red-hot metallic iron, or by dissolving iron in hydrochloric acid. The latter solution yields, when duly concentrated, green crystals of the hydrated dichloride, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, they are very soluble and deliquescent, and rapidly oxidize in the air.

The trichloride, or *Ferric chloride*, Fe_2Cl_6 , is usually prepared by dissolving ferric oxide in hydrochloric acid. The solution, evaporated to a syrupy consistence, deposits red hydrated crystals which are very soluble in water and alcohol. It forms double salts with potassium chloride and sal ammoniac. When evaporated to dryness and strongly heated, much of the chloride is decomposed yielding sesquioxide and hydrochloric acid; the remainder sublimes, and afterwards condenses in the form of small brilliant red crystals, which deliquesce rapidly. Anhydrous ferric chloride is also produced by the action of chlorine upon the heated metal. The solution of ferric chloride is capable of dissolving a large excess of recently precipitated ferric hydrate, by which it acquires a much darker color.

Iodides.—*Ferrous iodide*, FeI_2 , is an important medicinal preparation. It is easily made by digesting iodine with water and metallic iron. The solution is pale-green, and yields, on evaporation, crystals resembling those of the chloride, which rapidly oxidize on exposure to air. It is best preserved in solution in contact with excess of iron.—*Ferric iodide*, Fe_2I_6 , is yellowish-red and soluble.

Iron Oxides and Oxy-salts.—Three oxides of iron are known, namely, ferrous oxide, FeO , and ferric oxide, Fe_2O_3 , analogous to the chlorides, and an intermediate oxide, usually called magnetic iron oxide, containing Fe_3O_4 or $\text{FeO} \cdot \text{Fe}_2\text{O}_3$. A trioxide, FeO_3 , is supposed to exist in a class of salts called ferrates, but it has not been isolated.

Mono-oxide, or *Ferrous oxide*, FeO .—This is a very powerful base, neutralizing acids, and isomorphous with magnesia, zinc oxide, etc. It is almost unknown in the separate state, from its extreme proneness to absorb oxygen and pass into the sesquioxide. When a ferrous salt is mixed with caustic alkali or ammonia, a bulky whitish precipitate of ferrous hydrate falls, which becomes nearly black when boiled, the water being separated. This hydrate changes very rapidly when exposed to the air, becoming green and ultimately red-brown. The soluble ferrous salts have commonly a delicate pale-green color, and a nauseous metallic taste.

Sesquioxide, or *Ferric oxide*, Fe_2O_3 .—A feeble base, isomorphous with alumina. It occurs native, most beautifully crystallized as specular iron ore, in the island of Elba, and elsewhere; also as red and brown *limonite*,

the latter being a hydrate. It is artificially prepared by precipitating a solution of ferric sulphate or chloride with excess of ammonia, and washing, drying, and igniting the yellowish-brown hydrate thus produced: fixed alkali must not be used in this operation, as a portion is retained by the oxide. In fine powder, this oxide has a full red color, and is used as a pigment, being prepared for the purpose by calcination of ferrous sulphate, the tint varies somewhat with the temperature to which it has been exposed. The oxide is unaltered in the fire, although easily reduced at a high temperature by carbon or hydrogen. It dissolves in acids, with difficulty after strong ignition, forming a series of reddish salts, which have an acid reaction and an astringent taste. Ferric oxide is not acted upon by the magnet.

Triferro-tetroxide, Ferroso-ferric oxide, $\text{Fe}_3\text{O}_4 = \text{FeO} \cdot \text{Fe}_2\text{O}_3$, also called black iron oxide, magnetic oxide, and lodestone, a natural product, one of the most valuable of the iron-ores, often found in regular octohedral crystals, which are magnetic. It may be prepared by mixing due proportions of ferrous and ferric salts, precipitating them with excess of alkali, and then boiling the mixed hydrates; the latter then unite to a black sandy substance, consisting of minute crystals of the magnetic oxide. This oxide is the chief product of the oxidation of iron at a high temperature in the air and in aqueous vapor. It is incapable of forming definite salts.

FERRATES.—When a mixture of one part of pure ferric oxide and four parts of dry nitre is heated to full redness for an hour in a covered crucible, and the resulting brown, porous, deliquescent mass is treated when cold with ice-cold water, a deep amethystine-red solution of potassium ferrate is obtained. The same salt may be more easily prepared by passing chlorine gas through a strong solution of potash in which recently precipitated ferric hydrate is suspended; it is then deposited as a black powder, which may be drained upon a tile. It consists of K_2FeO_4 or $\text{K}_2\text{O} \cdot \text{FeO}_3$, and is therefore analogous in composition to the sulphate and chromate of potassium. The solution of this salt gradually decomposes, even in the cold, and rapidly when heated, giving off oxygen and depositing sesquioxide. The solution of potassium ferrate gives no precipitate with salts of calcium, magnesium, or strontium, but when mixed with a barium salt, it yields a deep crimson, insoluble *barium ferrate*, BaFeO_4 or $\text{BaO} \cdot \text{FeO}_3$, which is very permanent. Neither the hydrogen-salt or ferric acid, H_2FeO_4 , nor the corresponding anhydrous oxide, FeO_3 , is known in the separate state.

Ferrous Sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{FeO} \cdot \text{SO}_3 \cdot 7\text{H}_2\text{O}$.—This beautiful and important salt, commonly called *green vitriol*, *iron vitriol*, or *copperas*, may be obtained by dissolving iron in dilute sulphuric acid: it is generally prepared, however, and on a very large scale, by contact of air and moisture with common iron pyrites, which, by absorption of oxygen, readily furnishes the substance in question. Heaps of this material are exposed to the air until the decomposition is sufficiently advanced: the salt produced is then dissolved out by water, and the solution made to crystallize. It forms large green crystals, of the composition above stated, which slowly effloresce and oxidize in the air: it is soluble in about twice its weight of cold water. Crystals containing 4 and also 2 molecules of water have been obtained. Ferrous sulphate forms double salts with the sulphates of potassium and ammonium, containing $\text{Fe} \cdot \text{K}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, isomorphous with the corresponding magnesium salts.

Ferric Sulphate, $(\text{Fe})^2(\text{SO}_4)_3$ or $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$, is prepared by adding to a solution of the ferrous salt exactly one-half as much sulphuric acid as

it already contains, raising the liquid to the boiling-point, and then dropping in nitric acid until the solution ceases to blacken by such addition. The red liquid thus obtained furnishes, on evaporation to dryness, a buff-colored amorphous mass, which dissolves very slowly when put into water. With the sulphates of potassium and ammonium, this salt yields compounds having the form and constitution of alums; the potassium salt, for example, has the composition $\text{Fe}'''\text{K}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$. The crystals are nearly destitute of color; they are decomposed by water, and sometimes by long keeping in the dry state. These salts are best prepared by exposing to spontaneous evaporation a solution of ferric sulphate to which potassium or ammonium sulphate has been added.

FERROUS NITRATE, $\text{Fe}(\text{NO}_3)_2$.—When dilute cold nitric acid is made to act to saturation upon iron monosulphide, and the solution is evaporated in a vacuum, pale-green and very soluble crystals of ferrous nitrate are obtained, which are very subject to alteration. Ferric nitrate is readily formed by pouring nitric acid, slightly diluted, upon iron: it is a deep-red liquid, apt to deposit an insoluble basic salt, and is used in dyeing.

FERROUS CARBONATE, FeCO_3 or $\text{FeO} \cdot \text{CO}_2$.—The whitish precipitate obtained by mixing solutions of ferrous salt and alkaline carbonate: it cannot be washed and dried without losing carbonic acid and absorbing oxygen. This substance occurs in nature as *spathose iron ore*, or *iron spar*, associated with variable quantities of calcium and magnesium carbonates; also in the common *clay iron-stone*, from which nearly all the British iron is made. It is often found in mineral waters, being soluble in excess of carbonic acid: such waters are known by the rusty matter they deposit on exposure to the air. No ferric carbonate is known.

The phosphates of iron are all insoluble.*

Iron Sulphides.—Several compounds of iron and sulphur are known: of these the two most important are the following. The *monosulphide*, or *ferrous sulphide*, FeS , is a blackish brittle substance, attracted by the magnet, formed by heating together iron and sulphur. It is dissolved by dilute acids, with evolution of sulphuretted hydrogen gas, and is constantly employed for that purpose in the laboratory, being made by projecting into a red-hot crucible a mixture of $2\frac{1}{2}$ parts of sulphur and 4 parts of iron filings or borings of cast iron, and excluding the air as much as possible. The same substance is formed when a bar of white-hot iron is brought in contact with sulphur. The *bisulphide*, FeS_2 , or iron pyrites, is a natural product, occurring in rocks of all ages, and evidently formed in many cases by the gradual deoxidation of ferrous sulphate by organic matter. It has a brass-yellow color, is very hard, not attracted by the magnet, and not acted upon by dilute acids. When it is exposed to heat, sulphur is expelled, and an intermediate sulphide, Fe_2S_3 , analogous to the black oxide, is produced. This substance also occurs native, under the

* Triferrous orthophosphate $\text{Fe}_3\text{P}_2\text{O}_8 \cdot \text{Aq}$, may be prepared from disodic orthophosphate and ferrous sulphate, their solutions having been previously deprived of air by boiling. The precipitate must be washed and dried out of contact of air. It is a white powder, insoluble in cold water, soluble in dilute mineral acids, and slightly in carbonic and dilute acetic acid. Ammonia dissolves it, forming a yellow solution, becoming turbid on exposure to the air. When the recent precipitate is washed and dried with exposure to the air, it is oxidized, becoming blue, passing to the ferroso-ferric orthophosphate containing $2\text{Fe}_2\text{P}_2\text{O}_8 \cdot \text{Fe}_2\text{O}_3 \cdot \text{PO}_4 \cdot \text{Aq}_{10}$.

Ferric pyrophosphate, $\text{Fe}_2\text{P}_2\text{O}_7 \cdot \text{Aq}_{10}$, is prepared by precipitating neutral ferric chloride by sodium pyrophosphate. White powder, insoluble in water, soluble in acids, solution of sodium phosphate, ammonia, and its carbonates. R. B.

name of *magnetic pyrites*. Iron pyrites is the material now chiefly employed for the manufacture of sulphuric acid; for this purpose the mineral is roasted in a current of air, and the sulphurous acid formed is passed into the lead chambers; the residue consists of iron oxide, frequently containing a quantity of copper large enough to render the extraction of that metal remunerative.

Compounds of iron with *phosphorus*, *carbon*, and *silicon* exist, but little is known respecting them in a definite state. The carbonide is contained in cast iron and in steel, to which it communicates ready fusibility; the silico-compound is also found in cast iron. Phosphorus is a very hurtful substance in bar iron, as it renders it brittle or *cold-short*.

REACTIONS OF IRON SALTS.—**Ferrous salts** are thus distinguished:—

Caustic alkalis and *ammonia* give nearly white precipitates, insoluble in excess of the reagent, rapidly becoming green, and ultimately brown, by exposure to air. The *carbonates* of *potassium*, *sodium*, and *ammonium* throw down whitish ferrous carbonate, also very subject to change. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down black ferrous sulphide, soluble in dilute acids. *Potassium ferrocyanide* gives a nearly white precipitate, becoming deep-blue on exposure to air; the *ferricyanide* gives at once a deep-blue precipitate.

Ferrie salts are thus characterized:—

Caustic fixed alkalis and *ammonia* give foxy-red precipitates of ferric hydrate, insoluble in excess.

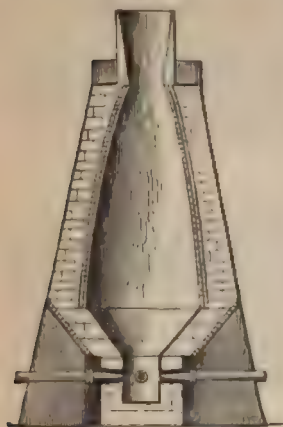
The *carbonates* behave in a similar manner, the carbonic acid escaping. *Hydrogen sulphide* gives a nearly white precipitate of sulphur, and reduces the sesquioxide to monoxide. *Ammonium sulphide* gives a black precipitate, slightly soluble in excess. *Potassium ferrocyanide* yields Prussian blue. Tincture or infusion of *gall-nuts* strikes intense bluish-black with the most dilute solutions of ferric salts.

Iron Manufacture.—This most important branch of industry consists, as now conducted, of two distinct parts—viz., the production from the ore of a fusible carbonide of iron, and the subsequent decomposition of the carbonide, and its conversion into pure or malleable iron.

The clay-iron ore is found in association with coal, forming thin beds or nodules: it consists, as already mentioned, of ferrous carbonate mixed with clay; sometimes lime and magnesia are also present. It is broken in pieces, and exposed to heat in a furnace resembling a lime-kiln, by which the water and carbonic acid are expelled, and the ore rendered dark-colored, denser, and also magnetic: it is then ready for reduction. The furnace in which this operation is performed is usually of very large dimensions, 50 feet or more in height, and constructed of brickwork with great solidity, the interior being lined with excellent fire-bricks: the shape will be understood from the section shown in fig. 159. The furnace is close at the bottom, the fire being maintained by a powerful artificial blast introduced by two or three *twegere-pipes*, as shown in the section. The materials, consisting of due proportion of coke or carbonized coal, roasted ore, and limestone, are constantly supplied from the top, the operation proceeding continuously night and day often for years, or until the

furnace is judged to require repair. In the upper part of the furnace, where the temperature is still very high, and where combustible gases

Fig. 169.



abound, the iron of the ore is probably reduced to the metallic state, being disseminated through the earthy matter of the ore. As the whole sinks down and attains a still higher degree of heat, the iron becomes converted into carbonide by *cementation*, while the silica and alumina unite with the lime, purposely added, to a kind of glass or *slag*, nearly free from iron oxide. The carbonide and slag, both in a melted state, reach at last the bottom of the furnace, where they arrange themselves in the order of their densities: the slag flows out at certain apertures contrived for the purpose, and the iron is discharged from time to time, and suffered to run into rude moulds of sand by opening an orifice at the bottom of the recipient, previously stopped with clay. Such is the origin of *crude*, *cast*, or *pig iron*, of which there are several varieties, distinguished by differences of color, hardness, and composition, and known by the names of *gray*, *black*, and *white iron*. The first is

for most purposes the best, as it admits of being filed and cut with perfect ease. The black and gray kinds probably contain a mechanical admixture of graphite, which separates during solidification.

A great improvement in the original mode of conducting the process was the substitution of raw coal for coke, and the blowing of hot air instead of cold into the furnace. This is effected by causing the air, on leaving the blowing-machine, to circulate through a system of red-hot iron pipes, until its temperature becomes high enough to melt lead. This alteration effects a prodigious saving in fuel, without injury to the quality of the product.

The conversion of cast-into bar-iron is effected chiefly by an operation called *puddling*, previous to which, however, it sometimes undergoes a process called *refining*, which consists in remelting it, in contact with the fuel, in small low furnaces called *refineries*, while air is blown over its surface by means of *twyeres*. The effect of this operation is to deprive the iron of a great part of the carbon and silicon associated with it. The metal thus purified is run out into a trench, and suddenly cooled, by which it becomes white, crystalline, and exceedingly hard: in this state it is called *fine metal*. The puddling is conducted in an ordinary reverberatory furnace, into which the charge of crude or of fine metal is introduced by a side aperture. This is speedily melted by the flame, and its surface covered with a crust or oxide. The workman then, by the aid of an iron tool, diligently stirs the melted mass, so as intimately to mix the oxide with the metal; he now and then also throws in a little water, with the view of promoting more rapid oxidation. Small jets of blue flame soon appear upon the surface of the iron, and the latter, after a time, begins to lose its fluidity, and acquires, in succession, a pasty and a granular condition. At this point the fire is strongly urged, the sandy particles once more cohere, and the contents of the furnace now admit of being formed into several large balls or masses, which are then withdrawn, and placed under an immense hammer, moved by machinery, by which each becomes

the latter being a hydrate. It is artificially prepared by precipitating a solution of ferric sulphate or chloride with excess of ammonia, and washing, drying, and igniting the yellowish-brown hydrate thus produced: fixed alkali must not be used in this operation, as a portion is retained by the oxide. In fine powder, this oxide has a full red color, and is used as a pigment, being prepared for the purpose by calcination of ferrous sulphate; the tint varies somewhat with the temperature to which it has been exposed. The oxide is unaltered in the fire, although easily reduced at a high temperature by carbon or hydrogen. It dissolves in acids, with difficulty after strong ignition, forming a series of reddish salts, which have an acid reaction and an astringent taste. Ferric oxide is not acted upon by the magnet.

Tetraferro-tetroxide, Ferroso-ferric oxide, $\text{Fe}_3\text{O}_4 = \text{FeO} \cdot \text{Fe}_2\text{O}_3$, also called *black iron oxide, magnetic oxide*, and *loadstone*, a natural product, one of the most valuable of the iron-ores, often found in regular octohedral crystals, which are magnetic. It may be prepared by mixing due proportions of ferrous and ferric salts, precipitating them with excess of alkali, and then boiling the mixed hydrates; the latter then unite to a black sandy substance, consisting of minute crystals of the magnetic oxide. This oxide is the chief product of the oxidation of iron at a high temperature in the air and in aqueous vapor. It is incapable of forming definite salts.

FERRATE.—When a mixture of one part of pure ferric oxide and four parts of dry nitre is heated to full redness for an hour in a covered crucible, and the resulting brown, porous, deliquescent mass is treated when cold with ice-cold water, a deep amethystine-red solution of potassium ferrate is obtained. The same salt may be more easily prepared by passing chlorine gas through a strong solution of potash in which recently precipitated ferric hydrate is suspended; it is then deposited as a black powder, which may be drained upon a tile. It consists of K_2FeO_4 or $\text{K}_2\text{O} \cdot \text{FeO}_3$, and is therefore analogous in composition to the sulphate and chromate of potassium. The solution of this salt gradually decomposes, even in the cold, and rapidly when heated, giving off oxygen and depositing sesquioxide. The solution of potassium ferrate gives no precipitate with salts of calcium, magnesium, or strontium, but when mixed with a barium salt, it yields a deep crimson, insoluble *barium ferrate*, BaFeO_4 or $\text{BaO} \cdot \text{FeO}_3$, which is very permanent. Neither the hydrogen-salt or ferric acid, H_2FeO_4 , nor the corresponding anhydrous oxide, FeO_3 , is known in the separate state.

FERROUS SULPHATE, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{FeO} \cdot \text{SO}_3 \cdot 7\text{H}_2\text{O}$.—This beautiful and important salt, commonly called *green vitriol*, *iron vitriol*, or *copperas*, may be obtained by dissolving iron in dilute sulphuric acid: it is generally prepared, however, and on a very large scale, by contact of air and moisture with common iron pyrites, which, by absorption of oxygen, readily furnishes the substance in question. Heaps of this material are exposed to the air until the decomposition is sufficiently advanced: the salt produced is then dissolved out by water, and the solution made to crystallize. It forms large green crystals, of the composition above stated, which slowly effloresce and oxidize in the air: it is soluble in about twice its weight of cold water. Crystals containing 4 and also 2 molecules of water have been obtained. Ferrous sulphate forms double salts with the sulphates of potassium and ammonium, containing $\text{FeK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, isomorphous with the corresponding magnesium salts.

FERRIC SULPHATE, $(\text{Fe}_2)^{VI}(\text{SO}_4)_3$ or $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$, is prepared by adding to a solution of the ferrous salt exactly one-half as much sulphuric acid as

some substance capable of resisting the fire, and exposed for many hours to a full red heat. The iron takes up, under these circumstances, from 1.3 to 1.7 per cent. of carbon, becoming harder, and at the same time fusible, with a certain diminution, however, of malleability. The active agent in this cementation process is probably carbon monoxide: the oxygen of the air in the crucible combines with the carbon to form that substance, which is afterwards decomposed by the heated iron, one-half of its carbon being abstracted by the latter. The carbon dioxide thus formed takes up an additional dose of carbon from the charcoal, and again becomes monoxide, the oxygen, or rather the carbon dioxide, acting as a carrier between the charcoal and the metal. The product of this operation is called *blistered steel*, from the blistered and rough appearance of the bars: the texture is afterwards improved and equalized by welding a number of these bars together, and drawing the whole out under a light tilt-hammer.

Some chemists have recently asserted that nitrogen is necessary for the production of steel, and have, in fact, attributed to its presence the peculiar properties of this material; others, again, have disputed this assertion, and believe that the transformation of iron into steel depends upon the assimilation of carbon only; experimentally, the question remains undecided.

Excellent steel is obtained by fusing gray cast-iron with tungstic oxide; the carbon of the iron reduces the tungstic oxide to tungsten, which forms with the iron an alloy possessing the properties of steel. The quantity of tungsten thus absorbed by the iron is very small, and some chemists attribute the properties of the so-called tungsten steel to the general treatment rather than to the presence of tungsten.

The most perfect kind of steel is that which has undergone fusion, having been cast into ingot moulds, and afterwards hammered: of this all fine-cutting instruments are made. It is difficult to forge, requiring great skill and care on the part of the operator.

Steel may also be made directly from some particular varieties of cast-iron, as that from spathose iron ore containing a little manganese. The metal is retained, in a melted state, on the hearth of a furnace, while a stream of air plays upon it, and causes partial oxidation: the oxide produced reacts, as before stated, on the carbon of the iron, and withdraws a portion of that element. When a proper degree of stiffness or pastiness is observed in the residual metal, it is withdrawn, and hammered or rolled into bars. The *wootz*, or native steel of India, is probably made in this manner. Annealed cast-iron, sometimes called *run steel*, is now much employed as a substitute for the more costly products of the forge: the articles, when cast, are embedded in powdered iron ore, or some earthy material, and, after being exposed to a moderate red heat for some time, are allowed to cool slowly, by which a very great degree of softness and malleability is attained. It is very possible that some little decarbonization may take place during this process.

Cast-steel may also be made in Siemens's rotatory furnace above described, the balls being transferred from the rotator to the bath of a steel-melting furnace in their heated condition, and without subjecting them to previous consolidation under a hammer or shingling machine. It is possible, however, to push the operation within the rotator to the point of obtaining cast-steel. For this purpose the relative amount of carbonaceous matter is somewhat increased in the first instance, so that the ball, if shingled, would be of the nature of puddled steel, or even contain some carbon mechanically mixed.

Bessemer steel is produced by forcing atmospheric air into melted cast-iron. The carbon being oxidized more readily than the iron, it is converted into carbon monoxide, which escapes in a sufficiently heated state to take fire on coming in contact with atmospheric air. Considerable heat is gene-

the latter being a hydrate. It is artificially prepared by precipitating a solution of ferric sulphate or chloride with excess of ammonia, and washing, drying, and igniting the yellowish-brown hydrate thus produced: fixed alkali must not be used in this operation, as a portion is retained by the oxide. In fine powder, this oxide has a full red color, and is used as a pigment, being prepared for the purpose by calcination of ferrous sulphate: the tint varies somewhat with the temperature to which it has been exposed. The oxide is unaltered in the fire, although easily reduced at a high temperature by carbon or hydrogen. It dissolves in acids, with difficulty after strong ignition, forming a series of reddish salts, which have an acid reaction and an astringent taste. Ferric oxide is not acted upon by the magnet.

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FERRATES.—When a mixture of one part of pure ferric oxide and four parts of dry nitre is heated to full redness for an hour in a covered crucible, and the resulting brown, porous, deliquescent mass is treated when cold with ice-cold water, a deep amethystine-red solution of potassium ferrate is obtained. The same salt may be more easily prepared by passing chlorine gas through a strong solution of potash in which recently precipitated ferric hydrate is suspended; it is then deposited as a black powder, which may be drained upon a tile. It consists of K_2FeO_4 or $\text{K}_2\text{O} \cdot \text{FeO}_3$, and is therefore analogous in composition to the sulphate and chromate of potassium. The solution of this salt gradually decomposes, even in the cold, and rapidly when heated, giving off oxygen and depositing sesquioxide. The solution of potassium ferrate gives no precipitate with salts of calcium, magnesium, or strontium, but when mixed with a barium salt, it yields a deep crimson, insoluble *barium ferrate*, BaFeO_4 or $\text{BaO} \cdot \text{FeO}_3$, which is very permanent. Neither the hydrogen-salt or ferric acid, H_2FeO_4 , nor the corresponding anhydrous oxide, FeO_3 , is known in the separate state.

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FERRIC SULPHATE, $(\text{Fe})^{III}(\text{SO}_4)_3$ or $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$, is prepared by adding to a solution of the ferrous salt exactly one-half as much sulphuric acid as

precipitating a soluble nickel salt with caustic potash, and washing, drying, and igniting the apple-green hydrated oxide thrown down. It is an ashy-gray powder, freely soluble in acids, which it completely neutralizes, forming salts isomorphous with those of magnesium and the other members of the same group. Nickel salts, when hydrated, have usually a beautiful emerald-green color; in the anhydrous state they are yellow.

The *sesquioxide*, Ni_2O_3 , is a black insoluble substance, prepared by passing chlorine through the hydrated monoxide suspended in water, nickel chloride is then formed, and the oxygen of the oxide decomposed is transferred to a second portion. It is also produced when a salt of nickel is mixed with a solution of bleaching-powder. The sesquioxide is decomposed by heat, and evolves chlorine when treated with hot hydrochloric acid.

NICKEL SULPHATE, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.—This is the most important of the nickel salts. It forms green prismatic crystals, which require 3 parts of cold water for solution. Crystals with six molecules of water have also been obtained. It forms with the sulphates of potassium and ammonium beautiful double salts, $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, isomorphous with the corresponding magnesium salts.

When a strong solution of oxalic acid is mixed with sulphate of nickel, a pale bluish-green precipitate of oxalate falls after some time, very little nickel remaining in solution. The oxalate can thus be obtained for preparing the metal.

NICKEL CARBONATE, NiCO_3 .—When solutions of nickel sulphate or chloride and of sodium carbonate are mixed, a pale-green precipitate falls, which is a combination of nickel carbonate and hydrate. It is readily decomposed by heat.

Pure nickel salts are conveniently prepared on the small scale from crude speiss or kupfernickel by the following process: The mineral is broken into small fragments, mixed with from one-fourth to half its weight of iron filings, and the whole dissolved in nitro-muriatic acid. The solution is gently evaporated to dryness, the residue treated with boiling water, and the insoluble iron arsenate removed by a filter. The liquid is then acidulated with hydrochloric acid, treated with hydrogen sulphide in excess, which precipitates the copper, and, after filtration, boiled with a little nitric acid to bring back the iron to the state of sesquioxide. To the cold and largely diluted liquid solution, acid sodium carbonate is gradually added, by which the ferric oxide may be completely separated without loss of nickel salt. Lastly, the filtered solution, boiled with sodium carbonate in excess, yields an abundant pale-green precipitate of nickel carbonate, from which all the other compounds may be prepared.

The precipitate thus obtained may still, however, contain cobalt, the separation of which is not very easy. Several methods of separating these metals have been proposed, the best of which is perhaps that of H. Rose. The mixed oxides or carbonates being dissolved in excess of hydrochloric acid, the solution, largely diluted with water, is supersaturated with chlorine gas, whereby the cobalt monoxide is converted into sesquioxide, while the nickel monoxide remains unaltered. The liquid is next mixed with excess of recently precipitated barium carbonate, left to stand for twelve to eighteen hours, and shaken up from time to time. The whole of the cobalt is thereby thrown down as sesquioxide, while the nickel remains in solution, and may be precipitated as hydrate by potash, after the barium also contained in the solution has been removed by precipitation with sulphuric acid.*

* For other modes of separating nickel and cobalt, see Gmelin's Handbook, vol. v. pp. 366-381; and Watts's Dictionary of Chemistry, vol. i. 1046.

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and forms insoluble salts with all metals, except the alkali-metals and magnesium; 2. *Metatungstic acid*, which is soluble in water, and forms soluble salts with nearly all metals. Ordinary tungstic acid forms normal salts containing M_2WO_4 or $M_2O.WO_3$, and acid salts containing $3M_2O.7WO_3$, which may perhaps be regarded as double salts composed of diacid and triacid tungstates, that is, as $2(M_2O.2WO_3) + M_2O.3WO_3$. The tungstates of potassium and sodium, especially the latter, are sometimes used as mordants in dyeing, in place of stannates; also for rendering muslin and other light fabrics unflammable. Tungstous tungstate, $WO_2.WO_3$, which has the composition of *tungsten pentoxide*, W_2O_5 , is a blue substance formed by reducing tungstic oxide or tungstic acid with zinc and hydrochloric acid; also by heating ammonium tungstate to redness in a retort.

Metatungstates.—These salts, which have the composition of quadric acid tungstates, $M_2O.4WO_3$, are formed from ordinary tungstates by addition of tungstic acid, or by removing part of the base by means of an acid. They are for the most part soluble and crystallizable. By decomposing barium metatungstate with dilute sulphuric acid, and evaporating the filtrate in a vacuum, hydrated metatungstic acid is obtained in quadric octohedrous apparently containing $H_2O.4WO_3 + 31Aq.$; it is very soluble in water.

Silicotungstates.*—By boiling gelatinous silica with acid potassium tungstate, a crystalline salt is obtained, having the composition of a diacid potassium tungstate, $6(K_2O.2WO_3)$, or $K_{12}O_6.12WO_3$, in which one-third of the potassium is replaced by silicon, viz., $K_8SiO_6.12WO_3$, so that the silicon here enters as a *basylous* element. The resulting solution yields with mercurous nitrate a precipitate of *mercurous silicotungstate*: this, when decomposed by an equivalent quantity of hydrochloric acid, yields a solution of *hydrogen silicotungstate*, or *silicotungstic acid*; and the other silicotungstates, which are all soluble, are obtained by treating the acid with carbonates.

Silicodectungstic acid, $H_8SiO_6.10WO_3$, is obtained as an ammonium salt by boiling gelatinous silica with solution of acid ammonium tungstate; and from this, the acid and its other salts may be obtained in the same manner as the preceding. The silicodectungstates are very unstable, and the acid is decomposed by mere evaporation, depositing silica, and being converted into *tungstosilicic acid*, which is isomeric with silicotungstic acid, and likewise decomposes carbonates. All three of these acids are capable of exchanging either one-half or the whole of their basic hydrogen for metals, thereby forming acid and neutral salts; silicotungstic acid also forms an acid sodium salt in which only one-fourth of the hydrogen is replaced by sodium.

Tungsten Sulphides.—The *disulphide*, or *Tungstous sulphide*, WS_2 , is obtained in soft, black, needle-shaped crystals by igniting tungsten, or one of its oxides, with sulphur.

The *trisulphide*, or *Tungstic sulphide*, WS_3 , is formed by dissolving tungstic acid in ammonium sulphide, and precipitating with an acid, or by adding hydrochloric acid to the solution of an alkaline tungstate saturated with hydrogen sulphide. It is a light-brown precipitate, turning black when dry. It unites easily with basic metallic sulphides, forming the *sulphotungstates*, M_2WS_4 , analogous to the normal tungstates.

Reactions of Tungsten compounds.—Soluble tungstates, or metatungstates, supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic

* Margnac, Ann. Chim. Phys. [4] iii. 5; Watts's Dictionary of Chemistry, v. 915.

acid, yield, on the introduction of a piece of zinc, a beautiful blue color, arising from the formation of blue tungsten oxide. A soluble tungstate, mixed with ammonium sulphide, and then with excess of acid, yields a light-brown precipitate of tungstic sulphide, soluble in ammonium sulphide. Hydrogen sulphide does not precipitate the acidulated solution of a tungstate, but turns it blue, owing to the formation of the blue oxide. Ordinary tungstates give, with potassium ferrocyanide, after addition of hydrochloric acid, a brown flocculent precipitate, soluble in pure water free from acid; metatungstates give no precipitate. Acids, added to solutions of ordinary tungstates, throw down a white or yellow precipitate of tungstic acid; with metatungstates no precipitate is obtained.

All tungsten compounds form colorless beads with borax and phosphorus salt, in the outer blowpipe flame. With borax, in the inner flame, they form a yellow glass, if the quantity of tungsten is somewhat considerable, but colorless with a smaller quantity. With phosphorus salt in the inner flame they form a glass of a pure blue color, unless metallic oxides are present, which modify it; in presence of iron the glass is blood-red, but the addition of metallic tin renders it blue.

Steel, alloyed with a small quantity of tungsten, acquires extraordinary hardness. Wootz, or Indian steel, contains tungsten. Tungsten has also a remarkable effect on steel in increasing its power of retaining magnetism when hardened. A horse-shoe magnet of ordinary steel, weighing two pounds, is considered of good quality when it bears seven times its own weight; but, according to Siemens, a similar magnet made with steel containing tungsten may be made to carry twenty times its weight suspended from the armature.*

MOLYBDENUM.

Atomic weight, 96. Symbol, Mo.

This metal occurs in small quantity as sulphide, or *molybdenite*, and as lead molybdate, or *wulfenite*. Metallic molybdenum is obtained by exposing molybdic oxide in a charcoal-lined crucible to the most intense heat that can be obtained. It is a white, brittle, and exceedingly infusible metal, having a density of 8.6, and oxidizing, when heated in the air, to molybdic oxide.

Chlorides.—Molybdenum forms four chlorides, containing MoCl_2 , MoCl_3 , or Mo_2Cl_6 , MoCl_4 , and MoCl_5 , or $\text{Mo}_2\text{Cl}_{10}$.

The pentachloride is produced when metallic molybdenum (previously freed from oxide by ignition in hydrogen chloride) is heated for some time in a stream of dry chlorine gas.

The pentachloride, heated to about 250° in a stream of hydrogen, is reduced to the red, difficultly volatile trichloride, MoCl_3 , or Mo_2Cl_6 ; and this compound, heated to redness in an atmosphere of carbon dioxide free from oxygen, is resolved, according to the equation $\text{Mo}_2\text{Cl}_6 = \text{MoCl}_4 + \text{MoCl}_5$, into the yellow dichloride, which remains in the tube, and the brown tetrachloride, which sublimates or is carried forward by the stream of gas.

Of these four chlorides the pentachloride is the only one which crys-

* Journal of the Chemical Society, July, 1868. 2d Series, vol. vi. p. 264.

tallizes distinctly, and melts and volatilizes without decomposition. The pure pentachloride is black. Its vapor has a dark brown-red color. The sulphur-yellow dichloride, and the red trichloride, which is deceptively like amorphous phosphorus, have been obtained only in the amorphous state; the tetrachloride is an indistinctly crystalline brown sublimate. In an atmosphere of carbon dioxide, the dichloride bears a bright red heat without melting or volatilizing; the trichloride, under the same circumstances, is resolved into di- and tetrachloride, which, when again heated, splits up into pentachloride which sublimes, and trichloride which remains behind.

The di- and trichloride are quite permanent in the air at ordinary temperatures, and insoluble in water; the tetra- and pentachloride, on the other hand, are extremely susceptible of the action of oxygen, and more particularly of moisture.

The dichloride is insoluble in *nitric acid*, which, however, dissolves all the other chlorides. The dichloride dissolves easily in hot *hydrochloric acid*, with aid of heat, and crystallizes therefrom on cooling, in long, shining, yellow needles, $\text{Mo}_2\text{Cl}_4 \cdot 3\text{H}_2\text{O}$, which give off $2\text{H}_2\text{O}$ at 100° .*

The *bromides* of molybdenum correspond in composition with the chlorides; there is also an oxybromide containing $\text{Mo}^{\text{VI}}\text{Br}_2\text{O}_3$.

Fluorides.—Molybdenum forms three fluorides, MoF_3 , MoF_4 , and MoF_5 , which are obtained by dissolving the corresponding oxides in hydrofluoric acid. The *heptafluoride* is not known in the free state, but only in combination with basic metallic fluorides and molybdates; thus there is a potassium salt containing $\text{K}_2\text{MoO}_4 \cdot \text{K}_2\text{MoF}_6$.

Oxides.—Molybdenum forms the three oxides, MoO , MoO_2 , and MoO_3 , besides several oxides intermediate between the last two, which may be regarded as molybdic molybdates.

The *monoxide*, or *Molybdous oxide*, MoO , is produced by bringing the dioxide or trioxide, in presence of one of the stronger acids, in contact with any of the metals which decompose water. Thus, when zinc is immersed in a concentrated solution of an alkaline molybdate mixed with a quantity of hydrochloric acid sufficient to redissolve the precipitate first thrown down, zinc chloride and molybdous chloride are formed. The dark-colored solution thus obtained is mixed with a large quantity of caustic potash, which precipitates a black hydrated molybdous oxide, and retains the zinc oxide in solution. The freshly-precipitated hydrate is soluble in acids and ammonium carbonate; when heated in the air, it burns to dioxide, but when dried in a vacuum, it leaves the black anhydrous monoxide.

The *dioxide*, or *Molybdic oxide*, MoO_2 , is obtained in the anhydrous state by heating sodium molybdate with sal-ammoniac, the molybdic trioxide being reduced to dioxide by the hydrogen of the ammoniacal salt; or, in the hydrated state, by digesting metallic copper in a solution of molybdic acid in hydrochloric acid, until the liquid assumes a red color, and then adding a large excess of ammonia. The anhydrous dioxide is deep brown and insoluble in acids; the hydrate resembles ferric hydrate, and dissolves in acids, yielding red solutions. It is converted into molybdic acid by strong nitric acid.

Trioxide, MoO_3 .—To obtain this oxide (commonly called *Molybdic acid*), native molybdenum sulphide is roasted, at a red heat, in an open vessel, and the impure molybdic trioxide thence resulting is dissolved by ammonia. The filtered solution is evaporated to dryness, and the salt is taken up by water and purified by crystallization. It is, lastly, decomposed by

* Liechti and Kempt, Liebigs Annalen, c. lxi. 344.

heat, and the ammonia expelled. The trioxide may also be prepared by decomposing native lead molybdate with sulphuric acid. It is a white crystalline powder, fusible at a red heat, and slightly soluble in water. The solution contains *molybdic acid*, but this acid, or hydrate, is not known in the solid state. The trioxide is easily dissolved by alkalies, and forms two series of salts, viz., *normal or neutral molybdates*, R_2MoO_4 , or $R_2O.MoO_3$, and *anhydromolybdates*, or *bimolybdates*, $R_2MoO_4.MoO_3$, or $R_2O.2MoO_3$, the symbol R denoting a univalent metal. The neutral molybdates of the alkali-metals are easily soluble in water, and their solutions yield, with the stronger acids, a precipitate, either of a less soluble bimolybdate, or of the anhydrous trioxide. The other molybdates are insoluble, and are obtained by precipitation. *Lead Molybdate*, $PbMoO_4$, occurs native in yellow quadratic plates and octohedrons.

Sulphides.—Molybdenum forms three sulphides, MoS_2 , MoS_3 , and MoS_4 , the last two of which are acid sulphides, forming sulphur-salts. The *disulphide*, or *Molybdic sulphide*, MoS_2 , occurs native, as *molybdenite*, in crystalline laminar masses, or tabular crystals, having a strong metallic lustre and lead-gray color, and forming a gray streak on paper, like plumbago. The same compound is produced artificially by heating either of the higher sulphides, or by igniting the trioxide with sulphur. When roasted in contact with the air, it is converted into trioxide.

The *trisulphide*, MoS_3 , commonly called *Sulphomolybdic acid*, is obtained by passing hydrogen sulphide into a concentrated solution of an alkaline molybdate, and precipitating with an acid. It is a black-brown powder, which is dissolved slowly by alkalies, more easily by alkaline sulphides and sulphydrates, forming sulphur salts called *Sulphomolybdates*. Most of these salts have the composition R_2MoS_4 , or $R_2S.MoS_3$, analogous to that of the molybdates. The sulpho-molybdates of the alkali-metals, alkaline earth-metals, and magnesium, are soluble in water, forming solutions of a fine red color; the rest are insoluble.

Tetrasulphide, MoS_4 .—This is also an acid sulphide, forming salts called *persulphomolybdates*, the general formula of which is R_2MoS_5 , or $R_2S.MoS_4$. The *potassium salt* is obtained by boiling the sulphomolybdate with molybdenum trisulphide.

Molybdous salts, obtained by dissolving molybdous oxide in acids, are opaque and almost black. They yield, with *hydrogen sulphide*, a brown-black precipitate soluble in ammonium sulphide; with *alkalies*, and *alkaline carbonates*, a brownish-black precipitate of molybdous hydrate, easily soluble in acid potassium carbonate, or in ammonium carbonate; with *potassium ferrocyanide*, a dark brown precipitate; with *sodium phosphate*, a white precipitate.

Solutions of molybdic salts have a reddish-brown color. When heated in the air, they have a tendency to become blue by oxidation. In contact with metallic zinc, they first blacken and then yield a black precipitate of molybdous hydrate. Their reactions with *alkalies*, *hydrogen sulphide*, etc., are similar to those of molybdous salts; but the precipitates are lighter in color.

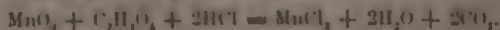
Molybdates are colorless unless they contain a colored base. Solutions of the alkaline molybdates yield with *acids* a precipitate of molybdic trioxide, soluble in excess of the precipitant. They are colored yellow by *hydrogen sulphide*, from formation of a sulpho-molybdate of the alkali-metal, and then yield with acids a brown precipitate of molybdenum trisulphide. This is an extremely delicate test for molybdic acid. They form white precipitates with the salts of the *earth-metals*, and precipitates of various colors with salts of the *heavy metals*. When *ortho-phosphoric acid*, or a liquid

Monoxide, or Manganous oxide, MnO.—When manganese carbonate is heated in a stream of hydrogen gas, or vapor of water, carbon dioxide is disengaged, and a greenish powder left behind, which is the monoxide. Prepared at a dull red heat only, the monoxide is so prone to absorb oxygen from the air, that it cannot be removed from the tube without change; but when prepared at a higher temperature, it appears more stable. This oxide is a very powerful base, being isomorphous with magnesia and zinc oxide; it dissolves quietly in dilute acids, neutralizing them completely, and forming salts, which have often a beautiful pink color. When alkalis are added to solutions of these compounds, the white hydrated oxide first precipitated speedily becomes brown by passing into a higher state of oxidation.

Sesquioxide, or Manganic oxide, Mn₂O₃.—This compound occurs in nature as *braunite*, and in the state of hydrate as *manganite*; a very beautiful crystallized variety is found at Ilfeld, in the Harz. It is produced artificially, by exposing the hydrated monoxide to the air, and forms the principal part of the residue left in the iron retort when oxygen gas is prepared by exposing the native dioxide to a moderate red heat. The color of the sesquioxide is brown or black, according to its origin or mode of preparation. It is a feeble base, isomorphous with alumina: for when gently heated with diluted sulphuric acid, it dissolves to a red liquid, which, on the addition of potassium or ammonium sulphate, deposits octohedral crystals, having a constitution similar to that of common alum: these are, however, decomposed by water. Strong nitric acid resolves this oxide into a mixture of monoxide and dioxide, the former dissolving, and the latter remaining unaltered: while hot oil of vitriol destroys it by forming manganeous sulphate and liberating oxygen gas. On heating it with hydrochloric acid, chlorine is evolved, as with the dioxide, but in smaller amount.

Dioxide, MnO₂.—*Peroxide of Manganese. Pyrolusite.*—The most common ore of manganese; it is found both massive and crystallized. It may be obtained artificially in the anhydrous state by gently calcining the nitrate, or in combination with water, by adding solution of bleaching powder to a salt of the monoxide. Manganese dioxide has a black color, is insoluble in water, and refuses to unite with acids. It is decomposed by hot hydrochloric acid and by oil of vitriol in the same manner as the sesquioxide. It unites with the stronger bases, potash, lime, etc., forming salts called *manganites*, e.g., $\text{CaO} \cdot \text{MnO}_2$ or CaMnO_3 , which are produced by precipitating a solution of a manganeous salt with the corresponding base in presence of an oxidizing agent, such as a stream of air or oxygen gas. Such are the *manganites* of calcium and magnesium formed in Weldon's process for the recovery of manganese dioxide from waste chlorine-liquors (p. 176). According to Frémy,* manganese dioxide likewise acts as a base, forming definite salts with acids, e.g., a sulphate, $\text{MnO}_2 \cdot \text{SO}_3$.

The proportion of real dioxide contained in a commercial sample of the black oxide may be determined as follows: 50 grains of the mineral, reduced to very fine powder, are put into the little vessel employed in the analysis of carbonates (p. 310), together with about half an ounce of cold water, and 100 grains of strong hydrochloric acid; 50 grains of crystallized oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, are then added, the cork carrying the drying tube is fitted, and the whole quickly weighed or counterpoised. The application of a gentle heat suffices to determine the action: the oxalic acid is oxidized into water and carbon dioxide, which escapes as gas, while the manganese remains in solution as manganeous chloride:



* *Comptes Rendus*, lxxxi. 1231; *Chem. Soc. Journal*, 1877, i. 32.

This equation shows that every two molecules of carbon dioxide evolved correspond with one molecule of manganese dioxide decomposed. Now the molecular weight of this oxide, 87, is so nearly equal to twice that of carbon dioxide, 44, that the loss of weight suffered by the apparatus when the reaction has become complete, and the residual gas has been driven off by momentary ebullition, may be taken to represent the quantity of real dioxide in the 50 grams of the sample. The apparatus of Will and Fresenius, described at page 311, may also be used with advantage in this process.

Peroxy-manganese-tetroxide, or *Red manganese oxide*, Mn_2O_4 , or probably Mn_2O_5 .—This oxide is also found native, as *hausmannite*, and is produced artificially by heating the dioxide or sesquioxide to whiteness, or by exposing the monoxide or carbonate to a red heat in an open vessel. It is a reddish-brown substance, incapable of forming salts, and acted upon by acids in the same manner as the two other oxides already described. Borax and glass in the fused state dissolve it, and acquire the color of the amethyst.

Varvicite, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{MnO} \cdot 3\text{MnO}_2 \cdot \text{H}_2\text{O}$, is a natural mineral, discovered by Phillips among certain specimens of manganese ore from Warwickshire: it has also been found at Hefeld in the Hartz. It much resembles the dioxide, but is harder and more brilliant. By a strong heat, varvicite is converted into red oxide, with disengagement of aqueous vapor and oxygen gas.

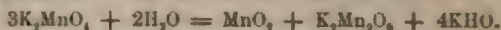
Several other oxides, intermediate in composition between the monoxide and dioxide, also occur native; they are probably mere mixtures, and in many cases the monoxide is more or less replaced by the corresponding oxides of iron, cobalt, and copper.

MANGANOUS SULPHATE, $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{MnO} \cdot \text{SO}_3 \cdot 7\text{H}_2\text{O}$.—A beautiful rose-colored and very soluble salt, isomorphous with magnesium sulphate. It is prepared on the large scale for the use of the dyer, by heating in a close vessel manganese dioxide and coal, and dissolving the impure monoxide thus obtained in sulphuric acid, with addition of a little hydrochloric acid towards the end of the process. The solution is evaporated to dryness, and again exposed to a red heat, by which ferrie sulphate is decomposed. Water then dissolves out the pure manganese sulphate, leaving ferrie oxide behind. The salt is used to produce a permanent brown dye, the cloth dyed in the solution being afterwards passed through a solution of bleaching powder, by which the monoxide is changed to insoluble hydrate of the dioxide. Manganoous sulphate sometimes crystallizes with 5 molecules of water. It forms a double salt with potassium sulphate, containing $\text{MnK}_2(\text{SO}_4)_4 \cdot 6\text{H}_2\text{O}$.

MANGANOUS CARBONATE, MnCO_3 or $\text{MnO} \cdot \text{CO}_2$.—Prepared by precipitating the dichloride with an alkaline carbonate. It is an insoluble white powder, sometimes with a buff-colored tint. Exposed to heat, it loses carbon dioxide and absorbs oxygen.

MANGANATES.—When an oxide of manganese is fused with potash, oxygen is taken up from the air, and a deep green saline mass results, which contains *potassium manganate*, K_2MnO_4 or $\text{K}_2\text{O} \cdot \text{MnO}_3$. The addition of potassium nitrate or chlorate facilitates the reaction. Water dissolves this compound very readily, and the solution, concentrated by evaporation in a vacuum, yields green crystals. *Barium manganate*, BaMnO_4 , is formed in a similar manner. In these salts manganese is sexvalent, like chromium in the chromates.

PERMANGANATES.—When potassium manganate, free from any great excess of alkali, is put into a large quantity of water, it is resolved into hydrated manganese dioxide, which subsides, and *potassium permanganate*, $K_2Mn_2O_8$ or $K_2O.Mn_2O_7$, which remains in solution, forming a deep purple liquid:



This effect is accelerated by heat. The changes of color accompanying this decomposition are very remarkable, and have procured for the manganate the name *mineral chameleon*; excess of alkali hinders the reaction in some measure, by conferring greater stability on the manganate. Potassium permanganate is easily prepared on a considerable scale. Equal parts of very finely powdered manganese dioxide and potassium chlorate are mixed with rather more than one part of potassium hydroxide dissolved in a little water, and the whole is exposed, after evaporation to dryness, to a temperature just short of ignition. The mass is treated with hot water, the insoluble oxide separated by decantation, and the deep-purple liquid concentrated by heat, until crystals form upon its surface: it is then left to cool. The crystals have a dark purple color, and are not very soluble in cold water. The manganates and permanganates are decomposed by contact with organic matter: the former are said to be isomorphous with the sulphates, and the latter with the perchlorates. The green and red disinfecting agents known as Condy's fluids, are alkaline manganates and permanganates.

Hydrogen permanganate, or *Permanganic acid*, $H_2Mn_2O_8$, is obtained by dissolving potassium permanganate in hydrogen sulphate, H_2SO_4 , diluted with one molecule of water, and distilling the solution at 60°C–70°C. Permanganic acid then passes over in violet vapors, and condenses to a greenish-black liquid, which has a metallic lustre, absorbs moisture greedily from the air, and acts as a most powerful oxidizing agent, instantly setting fire to paper and to alcohol. In this acid and its salts the manganese is septivalent (p. 241).

Manganous salts are very easily distinguished by reagents. The *fixed caustic alkalies* and *ammonia* give white precipitates, insoluble in excess, quickly becoming brown. The *carbonates of the fixed alkalies* and *carbonate of ammonia* give white precipitates, but little subject to change, and insoluble in excess of carbonate of ammonia. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down insoluble flesh-colored sulphide of manganese, which is very characteristic. *Potassium ferrocyanide* gives a white precipitate.

Manganese is also easily detected by the blowpipe: it gives with borax an amethyst-colored bead in the outer or oxidizing flame, and a colorless one in the inner flame. Heated upon platinum foil with sodium carbonate, it yields a green mass of sodium manganate.

CLASS VIII.—GROUP II.—PLATINUM METALS.

PLATINUM.

Atomic weight, 197.6. Symbol, Pt.

PLATINUM, palladium, rhodium, iridium, ruthenium, and osmium, form a group of metals, allied in some cases by properties in common, and still more closely by their natural association. *Crude platinum*, a native alloy of platinum, palladium, rhodium, iridium, and a little iron, occurs in grains and rolled masses, sometimes of tolerably large dimensions, mixed with gravel and transported materials, on the slope of the Ural Mountains in Russia, also in Brazil, Ceylon, and a few other places. It has never been seen in the rock, which, however, is judged from the accompanying materials to have been serpentine. It is stated to be always present in small quantities with native silver.

From this substance platinum is prepared by the following process: The crude metal is acted upon as far as possible by nitro-muriatic acid containing an excess of hydrochloric acid and slightly diluted with water, in order to dissolve as small a quantity of iridium as possible: to the deep yellowish-red and highly acid solution thus produced, sal-ammoniac is added, by which nearly the whole of the platinum is thrown down in the state of ammonium platinochloride. This substance, washed with a little cold water, dried, and heated to redness, leaves metallic platinum in the spongy state. This metal cannot be fused into a compact mass by ordinary furnace-heat, but the same object may be accomplished by taking advantage of its property of welding, like iron, at a high temperature. The spongy platinum is made into a thin uniform paste with water, introduced into a slightly conical mould of brass, and subjected to a graduated pressure, by which the water is squeezed out, and the mass rendered at length sufficiently solid to bear handling. It is then dried, very carefully heated to whiteness, and hammered, or subjected to powerful pressure. If this operation is properly conducted, the platinum will then be in a state to bear forging into a bar, which can afterwards be rolled into plates, or drawn into wire at pleasure.

A method of refining platinum has lately been devised by Deville and Debray. It consists in submitting the crude metal to the action of an intensely high temperature in a crucible of lime. The apparatus they employ is as follows: The lower part of the furnace consists of a piece of lime, hollowed out in the centre to the depth of about a quarter of an inch; a small notch is filed at one side of this basin, through which the metal is introduced and poured out. A cover made of another piece of lime fits on the top of this basin; it is also hollowed to a small extent, and has a conical perforation at the top, into which is inserted the nozzle of an oxyhydrogen blowpipe. The whole arrangement is firmly bound with iron wire. To use the apparatus, the stopcock supplying the hydrogen (or coal gas) is opened and the gas lighted at the notch in the crucible: the oxygen is then gradually supplied; and when the furnace is sufficiently hot, the metal is introduced in small pieces through the orifice. By this arrangement as much as 50 pounds of platinum and more may be fused at once. All the impurities in the platinum, except the iridium and rhodium, are

separated in this manner: the gold and palladium are volatilized; the sulphur, phosphorus, arsenic, and osmium, oxidized and volatilized; and the iron and copper oxidized and absorbed by the lime of the crucible.

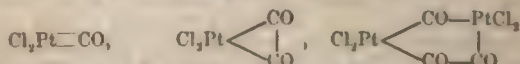
Platinum is a little whiter than iron: it is exceedingly malleable and ductile, both hot and cold, and is very infusible, melting only before the oxy-hydrogen blowpipe, or in the powerful blast furnace just described. It is the heaviest substance known, its specific gravity being 21.5. Neither air, moisture, nor the ordinary acids attack platinum in the slightest degree at any temperature: hence its great value in the construction of chemical vessels. It is dissolved by nitro-muriatic acid, and superficially oxidized by fused potassium hydroxide, which enters into combination with the oxide.

The remarkable property of the spongy metal to determine the union of oxygen and hydrogen has been already noticed. There is a still more curious state in which platinum can be obtained—that of *platinum-black*, in which the division is carried much further. It is easily prepared by boiling a solution of platonic chloride to which an excess of sodium carbonate and a quantity of sugar have been added, until the precipitate formed after a little time becomes perfectly black, and the supernatant liquid colorless. The black powder is collected on a filter, washed, and dried by gentle heat. This substance appears to possess the property of condensing gases, more especially oxygen, into its pores to a very great extent: when placed in contact with a solution of formic acid, it converts the latter, with copious effervescence, into carbonic acid; alcohol, dropped upon the platinum-black, becomes changed by oxidation to acetic acid, the rise of temperature being often sufficiently great to cause inflammation. When exposed to a red heat, the black substance shrinks in volume, assumes the appearance of common spongy platinum, and loses these peculiarities, which are no doubt the result of its excessively comminuted state.

Platinum forms two series of compounds: the *platinous* compounds, in which it is bivalent, *e. g.*, PtCl_2 , PtO , and the *platinoic* compounds, in which it is quadrivalent, *e. g.*, PtCl_4 , PtO_2 , etc.

Chlorides.—The *dichloride*, or *Platinous chloride*, PtCl_2 , is produced when platine chloride, dried and powdered, is exposed for some time to a heat of about 200° , whereby half the chlorine is expelled; also, when sulphurous acid gas is passed into a solution of the tetrachloride until the latter ceases to give a precipitate with sal-ammoniac. It is a greenish-gray powder, insoluble in water, but dissolved by hydrochloric acid. The latter solution, mixed with sal-ammoniac or potassium chloride, deposits a double salt in fine red prismatic crystals, containing, in the last case, $2\text{KCl}.\text{PtCl}_2$. The corresponding sodium compound is very soluble, and difficult to crystallize. These double salts are called *platinoschlorides* or *chloroplatinides*. Platinous chloride is decomposed by heat into chlorine and metallic platinum.

Platinous chloride unites with carbon monoxide, forming the three compounds



all of which are produced by heating platinous chloride in a stream of carbon monoxide. The first and third crystallize in yellow needles, the second in white needles.

Platinous chloride also unites with phosphorus trichloride, forming phospho-platinic chloride, $\text{Cl}_2\text{Pt}.\text{PCl}_3$, which is obtained by

heating spongy platinum with phosphorus pentachloride to 250°. It crystallizes in maroon-colored needles, melting at 170°. When heated with excess of phosphorus trichloride, it is converted in diphosphoplatinic chloride, $\text{Cl}_2\text{Pt} \begin{smallmatrix} \text{PCl}_2 \\ | \\ \text{PCl}_2 \end{smallmatrix}$, which forms canary-yellow crystals, melting at 160°. These two chlorides are converted by water—the latter on exposure to moist air at a low winter temperature—into phosphoplatinic and diphosphoplatinic acids, $\text{Cl}_2\text{Pt}=\text{P}(\text{OH})_2$ and $\text{Cl}_2\text{Pt} \begin{smallmatrix} \text{P}(\text{OH})_2 \\ | \\ \text{P}(\text{OH})_2 \end{smallmatrix}$, the former of which is tribasic, the latter sexbasic.

Platinum tetrachloride, or *Platinic chloride*, PtCl_4 , is always formed when platinum is dissolved in nitro-muriatic acid. The acid solution yields, on evaporation to dryness, a red or brown residue, deliquescent, and very soluble both in water and in alcohol; the aqueous solution has a pure orange-yellow tint. Platinic chloride unites with a great variety of metallic chlorides, forming double salts called *platio-chlorides* or *chloro-platinates*; the most important of these compounds are those containing the metals of the alkalis and ammonium. *Potassium platinochloride*, $2\text{KCl}.\text{PtCl}_4$, forms a bright yellow crystalline precipitate, being produced whenever solution of the chlorides of platinum and of potassium are mixed, or a potassium salt mixed with a little hydrochloric acid is added to platinum tetrachloride. It is feebly soluble in water, still less soluble in dilute alcohol, and is decomposed with some difficulty by heat. It is easily reduced by hydrogen at a high temperature, yielding a mixture of potassium chloride and platinum-black: the latter substance may thus, indeed, be very easily prepared. The *sodium salt*, $2\text{NaCl}.\text{PtCl}_4.6\text{H}_2\text{O}$, is very soluble, crystallizing in large, transparent, yellow-red prisms of great beauty. The *ammonium salt*, $2\text{NH}_4\text{Cl}.\text{PtCl}_4$, is undistinguishable, in physical characters, from the potassium-salt: it is thrown down as a precipitate of small, transparent, yellow, octohedral crystals when sal-ammoniac is mixed with platinic chloride; it is but feebly soluble in water, still less so in dilute alcohol, and is decomposed by heat, yielding spongy platinum, while sal-ammoniac, hydrochloric acid, and nitrogen are driven off. Platinic chloride also forms crystallizable double salts with the hydrochlorides of many organic bases; with ethylamine, for example, the compound, $2[\text{NH}_2(\text{C}_2\text{H}_5)]_2.\text{HCl}.\text{PtCl}_4$.

The *bromides* and *iodides* of platinum are analogous in composition to the chlorides, and likewise form double salts with alkaline bromides and iodides.

Oxides.—The *monoxide*, or *Platinous oxide*, PtO , is obtained by digesting the tetrachloride with caustic potash, as a black powder, soluble in excess of alkali. It dissolves also in acids with brown color, and the solutions are not precipitated by sal-ammoniac. When platinum dioxide is heated with solution of oxalic acid, it is reduced to monoxide, which remains dissolved. The liquid has a dark-blue color, and deposits fine copper-red needles of platinous oxalate.

The *dioxide*, or *Platinic oxide*, PtO_2 , is best prepared by adding barium nitrate to a solution of platinic sulphate; barium sulphate and platinic nitrate are then produced, and from the latter caustic soda precipitates one-half of the platinum as *platinic hydrate*. The sulphate is itself obtained by acting with strong nitric acid upon platinum bisulphide, which falls as a black powder when a solution of the tetrachloride is dropped into potassium sulphide. Platinic hydrate is a bulky brown powder, which, when gently heated, becomes black and anhydrous. It may also be formed by

boiling platinic chloride with great excess of caustic soda, and then adding acetic acid. It dissolves in acids, and combines with bases: the salts have a yellow or red tint, and a great disposition to unite with salts of the alkalis and alkaline earths, giving rise to a series of double compounds, which are not precipitated by excess of alkali. A combination of platinic oxide with ammonia exists, which is explosive. Both oxides of platinum are reduced to the metallic state by ignition.

Sulphides.—The compounds, PtS and PtS_2 , are produced by the action of hydrogen sulphide, or the hydrosulphide of an alkali-metal, on the dichloride and tetrachloride of platinum respectively; they are both black substances, insoluble in water. Platinic sulphide heated in a close vessel gives off half its sulphur, and is reduced to platinous sulphide. It dissolves in alkaline hydrates, carbonates, and sulphides, forming salts called *sulphoplatinates*, which are decomposed by acids.

Ammoniacal Platinum Compounds.—The chlorides, oxides, sulphates, etc., of platinum are capable of taking up two or more molecules of ammonia, and forming compounds analogous in many respects to the ammoniacal mercury compounds already described.

The nitrogen in all these compounds is quivalent, and consequently the groups *ammonia*, NH_3 , and *diammonia*, N_2H_4 or NH_2-NH_2 , or $NH_2(NH_2)$, are bivalent, having two free combining units.

The platinum in some of these compounds is bivalent (*plato* or *platose*), and unites by two of its combining units with the bivalent groups NH_2 or N_2H_4 , each of which retains one combining unite free. In others the platinum is quadrivalent (*platin*), and unites by some of its combining units with ammonia or diammonia, the remaining units being satisfied by combination with electro-negative radicles. In others, again, the platinum accumulates in such a manner as to form compounds containing $(Pt)_2^{IV}$, $(Pt^{IV}-Pt^{IV})^{IV}$, $(Pt^{IV}-Pt^{IV}-Pt^{IV}-Pt^{IV})^{IV}$, etc. The bivalent groups NH_2 , N_2H_4 , always go by pairs, excepting in the semi-diammoniums, in which half or a quarter of the combining units of the platinum is satisfied by once N_2H_4 .

The names and constitution of the several groups are given in the following table, the symbol R denoting a univalent chlorous radicle such as Cl , NO_2 , etc.

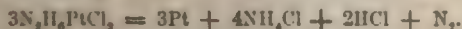
| | |
|-------------------------------------|---|
| 1. Platosammonium compounds, | $Pt \begin{smallmatrix} < NH_2R \\ < NH_2R \end{smallmatrix}$ |
| 2. Platosemidiammonium compounds, | $Pt \begin{smallmatrix} < NH_2(NH_2)R \\ < R \end{smallmatrix}$ |
| 3. Platomonodiammonium compounds, | $Pt \begin{smallmatrix} < NH_2(NH_2)R \\ < NH_2R \end{smallmatrix}$ |
| 4. Platosodiummonium compounds, | $Pt \begin{smallmatrix} < NH_2(NH_2)R \\ < NH_2(NH_2)R \end{smallmatrix}$ |
| 5. Platinammonium compounds, | $R_2Pt \begin{smallmatrix} < NH_2R \\ < NH_2R \end{smallmatrix}$ |
| 6. Platinosemidiammonium compounds, | $R_2Pt \begin{smallmatrix} < NH_2(NH_2)R \\ < R \end{smallmatrix}$ |
| 7. Platinomonodiammonium compounds, | $R_2Pt \begin{smallmatrix} < NH_2(NH_2)R \\ < NH_2R \end{smallmatrix}$ |

8. Platiodiammonium compounds, $R_2Pt \begin{smallmatrix} < NH_2(NH_4)R \\ < NH_2(NH_4)R \end{smallmatrix}$
9. Diplatinammonium compounds, $RPt \begin{smallmatrix} < NH_2R \\ < NH_2R \end{smallmatrix}$
 $RPt \begin{smallmatrix} < NH_2R \\ < NH_2R \end{smallmatrix}$
10. Diplatodiammonium compounds, $Pt-NH_2(NH_4)R$
 $Pt-NH_2(NH_4)R$
11. Diplatinodiammonium compounds, $R_2Pt-NH_2(NH_4)R$
 $R_2Pt-NH_2(NH_4)R$
12. Diplatinotetradiammonium compounds, $RPt \begin{smallmatrix} < NH_2(NH_4)R \\ < NH_2(NH_4)R \end{smallmatrix}$
 $RPt \begin{smallmatrix} < NH_2(NH_4)R \\ < NH_2(NH_4)R \end{smallmatrix}$

We shall here describe the most characteristic compounds of each group, referring for more complete description to larger works.*

1. *Plat ammonium Compounds*.—These compounds are formed by abstraction of the elements of ammonia, NH_3 , from the corresponding platodiammonium compounds. They are, for the most part, insoluble in water, but dissolve in ammonia, reproducing the platodiammonium compounds. They detonate when heated.

The *Chloride*, $Pt \begin{smallmatrix} < NH_2Cl \\ < NH_2Cl \end{smallmatrix}$, or $N_2H_6PtCl_2$, is formed by heating platodiammonium chloride to 220°–270°, or by heating the same salt with hydrochloric acid, or by boiling the green salt of Magnus (p. 444) with nitrate or sulphate of ammonium, and is deposited as a yellow crystalline powder, or in rhomboidal scales. It dissolves in 4472 parts of water at 0°, and in 120 parts of boiling water. At 270° it decomposes in the manner represented by the equation,



Silver nitrate added to its solution throws down all the chlorine. This salt is isomeric with the green salt of Magnus, with the yellow chloride of platodiammonium, and with the chloroplatinite of platomonodiammonium.

The corresponding *iodide*, $N_2H_6PtI_2$, is a yellow powder, obtained by heating the aqueous solution of the compound, $N_2H_6PtCl_2$. It dissolves in ammonia, reproducing the latter compound. The *oxide*, N_2H_6PtO , obtained by heating platodiammonium oxide (p. 444) to 110°, is a grayish mass, which, when heated to 100° in a close vessel, gives off water, ammonia, and nitrogen, and leaves metallic platinum. The *hydroxide*, $N_2H_6Pt.(HO)_2$, obtained by decomposing the sulphate with baryta-water, is a strong base, soluble in water, having an alkaline reaction, absorbing carbonic acid from the air, and liberating ammonia from its salts (Odling). The *sulphate*, $N_2H_6PtSO_4.H_2O$, and the *nitrate*, $N_2H_6Pt(NO_3)_2$, are obtained by boiling the *iodide* with sulphate and nitrate of silver: they are crystalline, and have

* See Watts's Dictionary of Chemistry, iv. 673, and 2d Suppl. 993.

a strong acid reaction. The sulphate retains a molecule of crystallization water, which cannot be removed without decomposing the salt.

2. *Platosesmidiammonium Compounds*.—These compounds, isomeric with the preceding, are formed by direct addition of ammonia to platinous salts. The chloride, $\text{Pt} \begin{smallmatrix} \text{N}_2\text{H}_6\text{Cl} \\ \text{Cl} \end{smallmatrix}$, is obtained by adding ammonia to a cold solution of platinous chloride in hydrochloric acid, filtering after 24 hours, and treating the yellowish-green residue with boiling water, which dissolves the platosesmidiammonium salt, and leaves the green salt of Magnus formed at the same time. The solution, on cooling, deposits the platosesmidiammonium chloride in small prisms, differing in form from the chloride above described, and much more soluble in water, requiring for solution 387 parts of cold, and 26 parts of boiling water. The other salts of this base are obtained by decomposing the chloride with the corresponding silver salts. The bromide and iodide crystallize in yellow needles; the nitrite in silky needles, which detonate when heated; the nitrate and sulphate form yellowish crystalline crusts.

3. *Platosomonodiammonium Compounds*, $\text{Pt} \begin{smallmatrix} \text{N}_2\text{H}_6\text{R} \\ \text{NH}_4\text{R} \end{smallmatrix}$.—The chloroplatinite of this series, $2\text{N}_2\text{H}_5\text{PtCl}_2 \cdot \text{PtCl}_2$, formed in small quantity on adding ammonia to a solution of platinous chloride, crystallizes in brown square laminae, slightly soluble in cold, more soluble in boiling water. Treated with silver nitrate it is converted into platosomonodiammonium nitrate, and this, when heated with hydrochloric acid, yields the corresponding chloride, $\text{N}_5\text{H}_9\text{PtCl}_2$, which is very soluble, and crystallizes in colorless needles, or nacreous scales.

4. *Platosodiammonium Compounds*, $\text{Pt} \begin{smallmatrix} \text{N}_2\text{H}_6\text{R} \\ \text{N}_2\text{H}_6\text{R} \end{smallmatrix}$.—The chloride, $\text{N}_4\text{H}_{12}\text{PtCl}_2$, one of the earliest discovered of the ammoniacal platinum compounds, is obtained by the action of ammonia on the green salt of Magnus, or on the chloride of platosammonium. When platinous chloride is boiled with excess of ammonia, till the green precipitate formed in the first instance is redissolved, a solution is obtained, which, when filtered and evaporated, yields the chloride of platosodiammonium in splendid yellow crystals containing one molecule of water, which they give off at 110° . It is soluble in water, and its solution mixed with platinous chloride yields platosodiammonium chloroplatinite, $\text{N}_4\text{H}_{12}\text{PtCl}_2 \cdot \text{PtCl}_2$, isomeric with platosammonium chloride, and constituting the green salt of Magnus, the first discovered of the ammonia-platinum compounds. This last salt may also be prepared by passing sulphurous acid gas into a boiling solution of platinic chloride, till it is completely converted into platinous chloride (and is therefore no longer precipitated by sal-ammoniac), and neutralizing the solution with ammonia. It forms dark-green needles, insoluble in water, alcohol, and hydrochloric acid.

The bromide and iodide of this series are obtained by treating the solution of the sulphate with bromide or iodide of barium: they crystallize in cubes. The oxide, $\text{N}_4\text{H}_{12}\text{PtO}$, is obtained as a crystalline mass by decomposing the solution of the sulphate with an equivalent quantity of baryta-water, and evaporating the filtrate in a vacuum. It is strongly alkaline and caustic, like potash, absorbs carbonic acid rapidly from the air, and precipitates silver oxide from the solution of the nitrate. It is a strong base, neutralizing acids completely, and expelling ammonia from its salts. It melts at 110° , giving off water and ammonia, and leaving platosammonium oxide. Its aqueous solution does not give off ammonia, even when boiled. The oxide absorbs carbon dioxide rapidly from the air, forming

first a neutral carbonate, $N_4H_{12}PtCO_3 \cdot H_2O$, and afterwards an acid salt, $N_4H_{12}PtCO_3 \cdot H_2CO_3$. The sulphate, $N_4H_{12}PtSO_4$, and the nitrate, $N_4H_{12}Pt(NO_3)_2$, are obtained by decomposing the chloride with silver sulphate or nitrate; they are neutral, and crystallize easily.

5. *Platinammonium Compounds*.—The chloride, $Cl_2Pt \begin{smallmatrix} \leftarrow NH_3Cl \\ \leftarrow NH_3Cl \end{smallmatrix}$, is obtained by the action of chlorine on platammonium chloride suspended in boiling water. It is a lemon-yellow crystalline powder, made up of octahedral crystals with truncated summits. It is insoluble in cold water, very slightly soluble in boiling water, or in water containing hydrochloric acid. It dissolves in ammonia at a boiling heat, and the solution, on cooling, deposits a yellow precipitate, consisting of platinodiammonium chloride. It dissolves in boiling potash without evolving ammonia.

Acetates.—An *oxynitrate*, $N_4H_6Pt(NO_3)_2O$, is obtained by boiling the chloride, $N_4H_6PtCl_4$, for several hours with a dilute solution of silver nitrate. It is a yellow crystalline powder, sparingly soluble in cold, more soluble in boiling water. The *normal nitrate*, $N_4H_6Pt(NO_3)_4$, is obtained by dissolving the oxynitrate in nitric acid: it is yellowish, insoluble in cold water, soluble in hot nitric acid.

The *oxide*, $N_4H_6PtO_2$, is obtained by adding ammonia to a boiling solution of platinammonium nitrate; it is then precipitated in the form of a heavy, yellowish, crystalline powder, composed of small shining rhomboidal crystals; it is nearly insoluble in boiling water, and resists the action of boiling potash. Heated in a close vessel, it gives off water and ammonia, and leaves metallic platinum. It dissolves readily in dilute acids, even in acetic acid, and forms a large number of crystallizable salts, both neutral and acid, having a yellow color, and sparingly soluble in water. Another compound of platonic oxide with ammonia, called *fulminating platinum*, whose composition has not been exactly ascertained, is produced by decomposing ammonium platino-chloride with aqueous potash. It is a straw-colored powder, which detonates slightly when suddenly heated, but strongly when exposed to a gradually increasing heat.

6. *Platinosemidiammonium Compounds*.—Isomeric with the preceding. The chloride, $Cl_2Pt \begin{smallmatrix} \leftarrow N_2H_5Cl \\ \leftarrow Cl \end{smallmatrix}$, formed by the action of chlorine on platinosemidiammonium chloride, crystallizes in yellow six-sided plates belonging to the rhombic system, turning green at 100° , and dissolving in potash without evolution of ammonia. A *basic nitrate*, $(OH)_2Pt \begin{smallmatrix} \leftarrow N_2H_5 \\ \leftarrow NO_2 \end{smallmatrix}$, is obtained as an amorphous yellow precipitate by treating the chloride with silver nitrate. A *chloronitrate*, $Cl_2Pt \begin{smallmatrix} \leftarrow N_2H_5 \cdot NO_2 \\ \leftarrow NO_2 \end{smallmatrix}$, obtained by the action of chlorine on platinosemidiammonium nitrate, crystallizes in small yellow needles.

7. *Platinomonodiammonium Compounds*.—The chloride, $Cl_2Pt \begin{smallmatrix} \leftarrow N_2H_5Cl \\ \leftarrow NH_3Cl \end{smallmatrix}$, formed by the action of nitro-muriatic acid on platinomonodiammonium chloride, crystallizes in rhombic or hexagonal plates. A *bromonitrate*, $Br_2Pt \begin{smallmatrix} \leftarrow N_2H_5(NO_2) \\ \leftarrow NH_3(NO_2) \end{smallmatrix} + H_2O$, obtained by adding bromine to the nitrate of platinomonodiammonium, forms yellow soluble crusts.

8. *Platinodiammonium Compounds*.—The chloride, $PtCl_2 \begin{smallmatrix} \leftarrow N_2H_5Cl \\ \leftarrow N_2H_5Cl \end{smallmatrix}$, is obtained by passing chlorine gas into a solution of pla-

diammonium chloride with bromine. A *basic nitrate*, $\text{HO} \begin{array}{c} \diagup \\ \text{Pt} \end{array} \begin{array}{c} \diagdown \\ \text{NO}_3 \end{array}$ is obtained by the action of nitric acid on platosediammonium, a white crystalline powder, converted by ammonia into the salt $(\text{N}_2\text{H}_6.\text{NO}_3)_2$. The *sulphatochloride*, $\text{Cl}_2\text{Pt} \begin{array}{c} \text{N}_2\text{H}_6 \\ \diagup \quad \diagdown \\ \text{N}_2\text{H}_6 \end{array} \text{SO}_4$, formed by the action of sulphuric acid on the chloride, crystallizes in slender needles. An *oxalochloride*, $\text{Cl}_2\text{Pt}(\text{N}_2\text{H}_6)_2(\text{C}_2\text{O}_4)$, obtained by treating the chloride with ammonium oxalate, is a very soluble crystalline powder.

9. *Diplatinammonium Iodide*, $\begin{array}{c} \text{IPt}(\text{NH}_3\text{I})_2 \\ | \\ \text{IPt}(\text{NH}_3\text{I})_2 \end{array}$, or $\text{I}_2(\text{Pt}_2)^{+1}(\text{N}_2\text{H}_6)^{-1}$

only term of this series at present known, is obtained by treating ammonium iodide with boiling potash, and the resulting yellow powder with hydriodic acid. It is a black amorphous substance, which again treated with potash and hydriodic acid yields the compound $(\text{NH}_3\text{I})_n$, and this by similar treatment may be converted into a more condensed compound $\text{I}_2(\text{Pt}_2)^{+10}(\text{NH}_3\text{I})_{10}$.

10. *Diplatosodiammonium Compounds*.—The *hydroxide*, $\text{Pt} \begin{array}{c} \text{N}_2\text{H}_6\text{—OH} \\ | \\ \text{Pt} \end{array} \begin{array}{c} \text{N}_2\text{H}_6\text{—OH} \\ | \\ \text{Pt} \end{array}$, formed by the action of caustic soda on the chloride of platosediammonium, is a grayish crystalline insoluble powder, which detonates violently when heated. Treated with hydrochloric acid, it yields a yellow powder, which is converted by boiling water into the chloride, $\text{Pt}_2(\text{N}_2\text{H}_6\text{Cl})_2$.

11. *Diplatinodiammonium Chloride*, $\begin{array}{c} \text{Cl}_2\text{Pt} \text{—} \text{NH}_3 \text{—} \text{NH}_3 \\ | \\ \text{Cl}_2\text{Pt} \text{—} \text{NH}_3 \text{—} \text{NH}_3 \end{array}$

low amorphous powder formed by the action of nitro-muriatic acid on the hydroxide of the preceding series.

$\text{BPt}(\text{N}_2\text{H}_6)$

ammoniac, and leaving metallic platinum. The nitric acid in this may be replaced by an equivalent quantity of carbonic or oxalic acid, to form the compounds, $N_6H_{24}Pt_2(CO_3)_4OCl_2$, and $N_6H_{24}Pt_2(C_2O_4)_2OCl_2$, which are crystallizable, and sparingly soluble. A *basic oxalate*, $N_6H_{24}Pt_2(C_2O_4)_4(NO_3)_2O$, insoluble in water, is obtained by adding ammon oxalate to the oxynitrate.

Reactions of Platinum Salts.—Platinic chloride, or a platinic oxygen-salt, may be recognized in solution by the yellow precipitate which it forms with *sal-ammoniac*, decomposable by heat, with production of spongy

platinous sulphide and ammonium sulphide gradually form a brown precipitate of platinic sulphide, soluble in excess of ammonium sulphide. Zinc dissolves metallic platinum.

Platinic chloride and sodium platinochloride are employed in analytical investigations to detect the presence of potassium and separate it from sodium. For the latter purpose, the alkaline salts are converted into chlorides, and in this state mixed with four times their weight of sodium chloride in crystals, the whole being dissolved in a little water. On the formation of the yellow salt appears complete, alcohol is added, the precipitate collected on a weighed filter, washed with weak spirit, dried, and weighed. The potassium chloride is then easily separated from the weight of the double salt; and this, subtracted from the weight of the mixed chlorides employed, gives that of the sodium chloride by difference; 100 parts of potassium platinochloride correspond to 851 parts of potassium chloride.

Crucibles and crucibles of platinum are of great value to the chemist: they are constantly used in mineral analysis for fusing siliceous substances with alkaline carbonates. They suffer no injury in this operation, but caustic alkali roughens and corrodes the metal. The experimenter must be particularly careful to avoid introducing any oxide of an fusible metal, as that of lead or tin, into a platinum crucible. If such an alloy should by any means occur, these metals will at once alloy themselves with the platinum, and the vessel will be destroyed. A platinum crucible must never be put naked into a coke or charcoal fire, but placed within a covered earthen crucible.

PALLADIUM.

Atomic weight, 106.6. Symbol, Pd.

From the solution of crude platinum, from which the greater part of metallic platinum has been precipitated by *sal-ammoniac*, is neutralized by sodium carbonate, and mixed with a solution of mercuric cyanide, on boiling, cyanide separates as a whitish insoluble substance, which, on being dried, and heated to redness, yields metallic palladium in a spongy state. The palladium may then be welded into a mass, in the manner as platinum.

Palladium closely corresponds with platinum in color and appearance; it is very malleable and ductile. Its density differs very much from platinum, being only 11.8. Palladium is more oxidable than platinum.

When heated to redness in the air, especially in the state of

sponge, it acquires a blue or purple superficial film of oxide, which is again reduced at a white heat. This metal is slowly attacked by nitric acid; its best solvent is nitro-muriatic acid.

Palladium, like platinum, forms two classes of compounds; namely, the palladious compounds, in which it is bivalent, and the palladic compounds, in which it is quadrivalent.

Chlorides.—The *dichloride*, or *Palladious chloride*, PdCl_2 , is obtained by dissolving the metal in nitro-muriatic acid, and evaporating the solution to dryness. It is a dark-brown mass, which dissolves in water if the heat has not been too great, and forms double salts with many metallic chlorides. The palladio-chlorides of ammonium and potassium are much more soluble than the corresponding platinochlorides: they have a brownish-yellow tint.

The *tetrachloride*, or *Palladic chloride*, PdCl_4 , exists only in solution and in combination with the alkaline chlorides. It is formed when the dichloride is digested in nitro-muriatic acid. The solution has an intense brown color, and is decomposed by evaporation. Mixed with potassium chloride, or with sal-ammoniac, it gives rise to a red crystalline precipitate, which is but little soluble in water.

Palladious Iodide, PdI_2 , is precipitated from the chloride or nitrate by soluble iodides, as a black mass, which gives off its iodine between 300° and 360° . Palladium-salts are employed for the quantitative estimation of iodine, chlorine and bromine not being precipitated by them.

Oxides.—The *monoxide*, or *Palladious oxide*, PdO , is obtained by evaporating to dryness, and cautiously heating the solution of palladium in nitric acid. It is black, and but little soluble in acids. The hydrate falls as a dark-brown precipitate when sodium carbonate is added to the above solution. It is decomposed by a strong heat.

The *dioxide*, or *Palladic oxide*, PdO_2 , is not known in the separate state. From a solution of palladic chloride, alkalis and alkaline carbonates throw down a brown precipitate, consisting of hydrated palladic oxide combined with the alkali. This compound gives off half its oxygen at a moderate heat, and the whole at a higher temperature. From hot solutions a black precipitate is obtained, containing the anhydrous dioxide. The hydrate dissolves slowly in acids, forming yellow solutions. In strong hydrochloric acid it dissolves without decomposition, forming *potassio-palladic chloride*, arising from admixed potash; with dilute hydrochloric acid, on the contrary, it gives off chlorine.

Pallidious Sulphide, PdS , is formed by fusing the metal with sulphur, or by precipitating a solution of a palladious salt with hydrogen sulphide. It is insoluble in ammonium sulphide.

Ammoniacal Palladium Compounds.—A moderately concentrated solution of palladium dichloride, treated with a slight excess of ammonia, yields a beautiful flesh-colored or rose-colored precipitate, consisting of $\text{N}_2\text{H}_6\text{Pd}^{++}\text{Cl}_2$. This precipitate dissolves in a large excess of ammonia, and the ammoniacal solution, when treated with acids, yields a yellow precipitate having the same composition. This yellow modification is likewise obtained by heating the red compound in the moist state to 1000° , or in the dry state to 2000° . The yellow compound dissolves abundantly in aqueous potash, forming a yellow solution, but without giving off ammonia, even when the liquid is heated to the boiling point; the red compound behaves in a similar manner, but, before dissolving, is converted into the yellow

modification. These compounds, discovered by Hugo Möller,* are analogous in their modes of formation, and probably therefore in constitution, to the two modifications of the platinum compound, $N_7H_6PtCl_2$ (p. 444); the red compound being *palladiosenad ammonium chloride*, $Pd\left\langle \begin{smallmatrix} NH_2 \\ Cl \end{smallmatrix} (NH_4)Cl \right\rangle$,

and the yellow compound, *palladammonium chloride*, $Pd\left\langle \begin{smallmatrix} NH_2 \\ NH_4 \end{smallmatrix} Cl \right\rangle$. The yellow compound, digested with water and silver oxide, yields *palladammonium oxide*, N_7H_6PdO , which is a strong base, soluble in water, having an alkaline taste and reaction, and absorbing carbonic acid from the air. *Palladiazonium sulphite*, $N_7H_6Pd.SO_3$, is formed by the action of sulphurous acid on the oxide or chloride; it crystallizes in orange-yellow octohedrons. The *sulphate*, *chloride*, *iodide*, and *bromide* have likewise been formed.

The compound $4NH_4PdCl_2$, *palladiodiammonium chloride*, $Pd[NH_2(NH_4)Cl]_2$, separates from an ammoniacal solution of palladammonium chloride in oblique rhombic prisms.

The *oxide*, N_7H_6PdO , obtained by decomposing the solution of this chloride with silver oxide, is also a strong base yielding crystallizable salts.

Palladious salts are well marked by the pale yellowish-white precipitate which they form with solution of mercuric cyanide. It consists of palladious cyanide, $PdCy_2$, and is converted by heat into the spongy metal.

Hydroiodic acid and *potassium iodide* throw down a black precipitate of palladium iodide, visible even to the 500,000th degree of dilution.

Palladium is readily alloyed with other metals, as copper; one of these compounds—namely, the alloy with silver—has been applied to useful purposes. An amalgam of palladium is now extensively used by dentists for stopping teeth.

A native alloy of gold with palladium is found in Brazil.

RHODIUM.

Atomic weight, 104.4. Symbol, Rh.

The solution from which platinum and palladium have been separated, in the manner already described, is mixed with hydrochloric acid, and evaporated to dryness. The residue is treated with alcohol, of specific gravity 0.837, which dissolves everything except the double chloride of rhodium and sodium. This is well washed with spirit, dried, heated to whiteness, and then boiled with water, whereby sodium chloride is dissolved out, and metallic rhodium remains. Thus obtained, rhodium is a white, coherent, spongy mass, still less fusible and less capable of being welded than platinum. Its specific gravity varies from 10.6 to 11.

Rhodium is very brittle: reduced to powder and heated in the air, it becomes oxidized, and the same alteration happens to a greater extent when it is fused with nitrate or bisulphate of potassium. None of the acids, singly or conjoined, dissolve this metal, unless it be in the state of alloy, as with platinum, in which state it is attacked by nitro-muriatic acid.

Rhodium forms but one chloride, containing $RhCl_3$, in which, like iron in ferric chloride, it may be regarded as either tri- or quadrivalent.

* Ann. Ch. Pharm. lxxxvi. 341.

This chloride is prepared by adding silicofluoric acid to the double chloride of rhodium and potassium, evaporating the filtered solution to dryness, and dissolving the residue in water. It forms a brownish-red deliquescent mass, soluble in water, with a fine red color. It is decomposed by heat into chlorine and metallic rhodium.

Rhodium and Potassium Chlorides.—The salt, $\text{RhCl}_3 \cdot 3\text{KCl} \cdot 3\text{H}_2\text{O}$, formed by mixing a solution of rhodic oxide in hydrochloric acid with a strong solution of potassium chloride, crystallizes in sparingly soluble efflorescent prisms. Another double salt, containing $\text{RhCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$, is prepared by heating in a stream of chlorine a mixture of equal parts of finely powdered metallic rhodium and potassium chloride. The salt has a fine red color, is soluble in water, and crystallizes in four-sided prisms. **Rhodium and sodium chloride**, $\text{RhCl}_3 \cdot 3\text{NaCl} \cdot 12\text{H}_2\text{O}$, is also a very beautiful red salt, prepared like the last. The *ammonium salt*, $\text{Rh}_2\text{Cl}_6 \cdot 6\text{NH}_4\text{Cl} \cdot 3\text{H}_2\text{O}$, obtained by decomposing the sodium salt with sal-ammoniac, crystallizes in fine rhombohedral prisms.

Rhodium Oxides.—Rhodium forms four oxides, containing RhO , Rh_2O_3 , RhO_2 , and RhO_3 .

The *monoxide*, RhO , is formed with incandescence, when the hydrated sesquioxide, $\text{Rh}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is heated in a platinum crucible. It is a dark gray substance, perfectly indifferent to acids.

The *sesquioxide*, or *rhodic oxide*, Rh_2O_3 , obtained by heating the nitrate, is a gray porous mass, with metallic iridescence; insoluble in acids, easily reduced by hydrogen. It forms two hydrates: $\text{Rh}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or RhH_2O_3 , obtained by precipitating a solution of rhodium and sodium chloride with potash in presence of alcohol, and $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ or $\text{RhH}_5\text{O}_3 \cdot \text{H}_2\text{O}$, formed by precipitating the same salt with aqueous potash.

The *dioxide*, RhO_2 , obtained by fusing pulverized rhodium or the sesquioxide with nitre and potash, and digesting the fused mass with nitric acid, to dissolve out the potash, is a dark brown substance, insoluble in acids. When chlorine is passed into a solution of rhodic pentahydrate, $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, a black-brown gelatinous precipitate of the trihydrate, $\text{Rh}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is formed at first; but this compound gradually loses its gelatinous consistence, becomes lighter in color, and is finally converted into a green hydrate of the dioxide, $\text{RhO}_2 \cdot 2\text{H}_2\text{O}$. The alkaline solution at the same time acquires a deep violet-blue color.

Trioxide, RhO_3 .—The blue alkaline solution above mentioned deposits, after a while, a blue powder, becoming green when dry, and yielding, when treated with nitric acid, a blue flocculent substance, consisting of the trioxide, easily reduced to the dioxide.

RHODIC SULPHATE, $\text{Rh}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, formed by oxidizing the sulphide with nitric acid, is a yellowish-white crystalline mass. *Potassio-rhodic sulphate*, $\text{RhK}(\text{SO}_4)_2$, is a reddish-yellow crystalline powder, formed by adding sulphuric acid to a solution of rhodium and potassium chloride.

Ammoniacal Rhodium Compounds.—An *ammonio-chloride*, 10NH_3 .

Rh_2Cl_6 , or $\begin{array}{c} \text{Cl}_2\text{Rh}-(\text{NH}_3)_5-\text{Cl} \\ | \\ \text{Cl}_2\text{Rh}-(\text{NH}_3)_5-\text{Cl} \end{array}$, is obtained as a yellow crystalline powder on mixing a dilute solution of rhodium and ammonium chloride with excess of ammonia, and leaving the filtered solution to evaporate. The corresponding oxide, $10\text{NH}_3 \cdot \text{Rh}_2\text{O}_3$, obtained by heating the chloride with silver oxide, is a strong base, from which the sulphate and oxalate may be obtained in crystalline form.

salts are, for the most part, rose-colored, and exhibit, in solution, the following reactions: with *hydrogen sulphide* and *ammonium sulphide*, a precipitate of rhodic sulphide, insoluble in excess of ammonium sulphide; with soluble *sulphites*, a pale yellow precipitate, affording a stannic reaction; with *potash*, a yellow precipitate of rhodic oxide, in excess; with *ammonia*, and with *alkaline carbonates*, a yellow precipitate after a while. No precipitate with alkaline chlorides or mercuric chloride. *Zinc* precipitates metallic rhodium.

Alloy of steel with a small quantity of rhodium is said to possess valuable properties.

[DAVYUM.

Atomic weight, 1. Symbol, Da.

It was discovered by Serge Kern in June, 1877, in platiniferous liquors named in honor of Sir Humphry Davy. It was obtained from the liquors left after the separation of platinum, palladium, and iridium by heating them with an excess of ammonium chloride. A deep-red precipitate was obtained, which, after calcination and heat, left a grayish mass resembling platinum sponge. This, fused in a hydrogen blowpipe, furnished 0.27 gramme of the fused metal. It is silver-white, hard, but malleable at a red heat; it is readily dissolved by aqua regia, and very slightly by boiling sulphuric acid. Its atomic weight is 9.30.

It has but one stable chloride. A second product containing more chlorine decomposes during the evaporation of the nitro-muriatic solution. It is soluble in water, alcohol, and ether, but not deliquescent. By heating the monoxide is formed.

It gives a bright yellow precipitate of hydrate, readily attacked by acetic acid. The hydrate dissolved in nitric acid gives a black mass, which, calcined, leaves a black product.

It forms with potassium cyanide a double cyanide left on solution in beautiful crystals. It forms double salts with potassium and sodium chlorides, which are insoluble in water, but highly soluble in alcohol. The double sodium salt has a characteristic reaction almost insoluble in water and alcohol. In acid solutions of davyum, heated hydrogen produces a precipitate of sulphide readily attacked by the sulphides.

Reaction of the chloride gives, with potassic sulphocyanide, a reaction similar to that of the ferric salts, a deep red color, and in concentrated solution a red precipitate; from hot solution by slow cooling large red crystals.

Its equivalent was at first supposed to be near 100, but some preliminary estimations made by M. Alexejeff have shown that it is probably 34.—R. B.]

IRIDIUM.

Atomic weight, 196. Symbol, Ir.

Crude platinum is dissolved in nitro-muriatic acid, a small quantity of gray, scaly, metallic substance usually remains behind, having resisted the action of the acid: this is a native alloy of iridium

and osmium, called *osmiridium* or *iridosmine*; it is reduced to powder, mixed with an equal weight of dry sodium chloride, and heated to redness in a glass tube, through which a stream of moist chlorine gas is transmitted. The further extremity of the tube is connected with a receiver containing solution of ammonia. The gas, under these circumstances, is rapidly absorbed, iridium chloride and osmium chloride being produced: the former remains in combination with the sodium chloride; the latter, being a volatile substance, is carried forward into the receiver, where it is decomposed by the water into osmic and hydrochloric acids, which combine with the alkali. The contents of the tube when cold are treated with water, by which the iridium and sodium chloride is dissolved out; this is mixed with an excess of sodium carbonate and evaporated to dryness. The residue is ignited in a crucible, boiled with water, and dried; it then consists of a mixture of ferric oxide and a combination of iridium oxide with soda: it is reduced by hydrogen at a high temperature, and treated successively with water and strong hydrochloric acid, by which the alkali and the iron are removed, while metallic iridium is left in a finely-divided state. By strong pressure and exposure to a white heat, a certain degree of compactness may be communicated to the metal.*

Iridium is a white brittle metal, fusible with great difficulty before the oxy-hydrogen blowpipe. Deville and Debray, by means of their powerful oxy-hydrogen blast furnace, have fused it completely into a pure white mass, resembling polished steel, brittle in the cold, somewhat malleable at a red heat, and having a density equal to that of platinum, viz., 21.15. By moistening the pulverulent metal with a small quantity of water, pressing it tightly, first between filtering paper, then very forcibly in a press, and calcining it at a white heat in a forge fire, it may be obtained in the form of a compact, very hard mass, capable of taking a good polish, but still very porous, and of a density not exceeding 16.0. After strong ignition it is insoluble in all acids, but when reduced by hydrogen at low temperatures, it oxidizes slowly at a red heat, and dissolves in nitro-muriatic acid. It is usually rendered soluble by fusing it with nitre and caustic potash, or by mixing it with common salt, or better, with a mixture of the chlorides of potassium and sodium, and igniting it in a current of chlorine, as above described.

Iridium forms three series of compounds, namely, the hypoiridious compounds, in which it is bivalent, as IrCl_2 , IrO ; the iridious compounds, in which it is trivalent or quadrivalent, e. g., IrCl_3 , or $\text{Ir}_2\text{Cl}_6 = \text{Cl}_3\text{Ir}-\text{IrCl}_3$; and the iridic compounds, in which it is also quadrivalent, as in IrCl_4 , IrO_2 , etc. It appears to be incapable of uniting with more than four atoms of a monad element.† It forms also a trioxide, IrO_3 , in which it is most probably sexvalent.

Chlorides.—Iridium appears to form three chlorides, but only two of them—namely, the trichloride and tetrachloride—have been obtained in definite form.

* *Osmiridium*, however, generally contains platinum, ruthenium, and other metals of the same group, which are not effectually separated by the method above described. The complete separation of the several metals of the platinum group has of late years formed the subject of several elaborate investigations, into which the limits of this work will not permit us to enter. (See *Watts's Dictionary of Chemistry*, li. 35; lv. 241, 689; v. 101, 124.)

† A hexachloride, IrCl_6 , was said by Berzelius to be obtained in combination with potassium chloride by fusing iridosmine with nitre, distilling the product with nitro-muriatic acid, and treating the residue with successive portions of water; but, according to Claus, the salt thus formed was really a ruthenium compound, having been prepared by Berzelius from iridosmine containing ruthenium.

The *dichloride*, IrCl_2 , is not known in the separate state, but appears to exist in certain double salts, called *hypochloriridites*.

The *trichloride*, or *Iridious chloride*, IrCl_3 , is prepared by strongly heating iridium with nitre, adding water and enough nitric acid to saturate the alkali, warming the mixture, and then dissolving the precipitated hydrate of the sesquioxide in hydrochloric acid; it forms a dark yellowish-brown solution. This substance combines with other metallic chlorides, forming compounds called *iridoso-chlorides*, or *chloriridites*, which may be prepared by reducing the corresponding chloriridates with sulphurous acid, hydrogen sulphide, or potassium ferrocyanide. Claus has obtained the compounds $\text{IrCl}_3 \cdot 3\text{NH}_4\text{Cl} \cdot 3\text{H}_2\text{O}$, $\text{IrCl}_3 \cdot 3\text{KCl} \cdot 3\text{H}_2\text{O}$, and $\text{IrCl}_3 \cdot 3\text{NaCl} \cdot 12\text{H}_2\text{O}$. They are olive-green pulverulent salts, soluble in water.

The *tetrachloride*, or *Iridic chloride*, IrCl_4 , is obtained in solution by dissolving very finely divided iridium, or one of its oxides, or the trichloride, in nitro-muriatic acid, and heating the liquid to the boiling point. On evaporating the solution, it remains in the form of a black, deliquescent amorphous mass, translucent with dark-red color at the edges; soluble, with reddish-yellow color, in water. It unites with alkaline chlorides, forming compounds called *iridochlorides*, or *chloriridates*, analogous in composition to the chloroplatinates. The ammonium salt, $\text{IrCl}_4 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$, and the potassium salt, $\text{IrCl}_4 \cdot 2\text{KCl}$, are formed, as dark-brown crystalline precipitates, on mixing the solutions of the component chlorides. The potassium salt may also be prepared by passing chlorine over a gently ignited and finely divided mixture of iridium with potassium chloride. It is soluble in boiling water, and crystallizes in black octohedrons, yielding a red powder. The sodium salt, $\text{IrCl}_4 \cdot 2\text{NaCl} \cdot 6\text{H}_2\text{O}$, prepared like the potassium salt, forms easily soluble black tables and prisms, isomorphous with the corresponding platinum salt.

Iodides.—Iridium forms three iodides, IrI_2 , IrI_3 , and IrI_4 , analogous to the chlorides, and yielding similar double salts with the iodides of the alkali-metals.*

Oxides.—Iridium forms four oxides, IrO , Ir_2O_3 , IrO_2 , and IrO_3 . The *monoxide*, or *hypoiridious oxide*, IrO , is but little known. It is obtained by precipitating an alkaline hypochloriridite with caustic alkali in an atmosphere of carbon dioxide; but on exposure to the air it is quickly converted into a higher oxide.

The *sesquioxide*, or *Iridious oxide*, Ir_2O_3 , was formerly regarded as the most easily formed and most stable of the oxides of iridium; but, according to Claus, it has a great tendency to take up oxygen and pass to the state of dioxide. It may be prepared by gently igniting a mixture of potassium chloriridite ($\text{IrCl}_3\text{KCl}_2$) with sodium carbonate in an atmosphere of carbon dioxide; on treating the product with water, the sesquioxide remains in the form of a black powder insoluble in acids. It forms two hydrates, $\text{Ir}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and $\text{Ir}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. It unites with bases, forming salts which may be called *iridites*. A solution of a chloriridite in excess of lime-water deposits, after standing for some time out of contact of air, a dirty yellow precipitate containing $3\text{CaO} \cdot \text{Ir}_2\text{O}_3$.

The *dioxide*, *Iridic oxide*, IrO_2 , is, according to Claus, the most easily prepared and most stable of all the oxides of iridium, and is always deposited in the form of a bulky, indigo-colored hydrate, $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$, when a solution of either of the chlorides of iridium or their double salts is boiled with an alkali; but it always retains 3 or 4 per cent. of the alkali. The hydrate may be obtained by dissolving the hydrated sesquioxide in potash and

* Offier, Ueber die Iodverbindungen des Iridiums. Göttingen, 1857.

treating the solution with an acid. It dissolves in acids, forming solutions which are dark-brown when concentrated, reddish-yellow when dilute.

The trioxide, or *Periridic oxide*, IrO_3 , is not known in the free state, but is formed in combination with potash, when iridium is fused for some time with nitre. The resulting blackish-green mass dissolves in water, forming a deep indigo-colored solution of basic potassium periridiate, leaving a black crystalline powder consisting of acid periridiate.*

Iridium, like the other platinum metals, shows but little tendency to form oxygen salts. The oxides dissolve in acids, but no definite salts are obtained in this way. The solution of iridic oxide in sulphuric acid has a dark-brown color, which is not modified by potash in the same manner as that of the dichloride, neither does it yield any blue precipitate on boiling.

The only definite oxygen-salts of iridium that have been obtained are double salts containing sulphurous and dithionic acids.

Hypo-iridoso-potassic Sulphite, $\text{IrSO}_3 \cdot 3\text{K}_2\text{SO}_3$, is obtained as a white crystalline powder, when the mother-liquor obtained in preparing potassium chloriridite by passing sulphurous oxide through a solution of the chloriridate, is evaporated to a small bulk.

Sulphides.—Three sulphides of iridium are known, analogous to the first three oxides above described. The *sesquisulphide* and *disulphide* are obtained as brown-black precipitates by treating the solutions of the trichloride and tetrachloride respectively with hydrogen sulphide. The *trisulphide* is a grayish-black substance obtained by decomposing either of the higher sulphides in a close vessel.

Ammoniacal Compounds of Iridium.—The *chlorides of iridosammonium* and *iridosodium*, $\text{Ir}(\text{NH}_4\text{Cl})_2$ and $\text{Ir}(\text{NH}_4(\text{NH}_4)\text{Cl})_2$, together with the corresponding sulphates, are prepared like the platinum compounds of analogous composition, which they also resemble in their properties. The *nitratochloride*, $\text{Ir} \left\langle \begin{smallmatrix} \text{NH}_4(\text{NH}_4)\text{NO}_3 \\ \text{NH}_4(\text{NH}_4)\text{Cl} \end{smallmatrix} \right\rangle$, is formed by heating the chloride, $\text{Ir}(\text{NH}_4\text{Cl})_2$, with strong nitric acid. *Iridiosammonium chloride*, $\text{Cl}_2\text{Ir}[\text{NH}_4(\text{NH}_4)\text{Cl}]_2$, is obtained as a violet precipitate by treating the nitrate just mentioned with hydrochloric acid.†

The compound, $10\text{NH}_4 \cdot \text{Ir}_2\text{Cl}_6$, analogous to the rhodium-compound above described (p. 450), but having no analogue in the platinum series, is obtained as a flesh-colored crystalline powder by prolonged digestion of ammonium chloriridate with warm aqueous ammonia. The corresponding carbonate, nitrate, and sulphate have also been prepared.‡

Iridic solutions (containing the dioxide or tetrachloride) are of a dark brown-red color; iridious solutions (containing the sesquioxide or trichloride) have an olive-green color. The characters of an iridic solution are best observed with sodium chloriridate, all the other iridic compounds being but slightly soluble.

Iridic solutions give with *ammonium* or *potassium chloride* a crystalline precipitate of ammonium or potassium chloriridate, which is distinguished from the corresponding platinum precipitate by its dark brown-red color, and further by its reduction to soluble chloriridite when treated with solution of hydrogen sulphide. This reaction serves for the separation of iridium from platinum.

* Claus, Ann. Ch. Pharm. lxx. 240.

† Skoblikoff, Ann. Ch. Pharm. lxxiv. 275.

‡ Claus, Beiträge zur Chemie der Platinmetalle. Dorpat, 1854.

RUTHENIUM.

Atomic weight, 104.4. Symbol, Ru.

This metal, discovered by Claus in 1846, occurs in platinum ore, and chiefly in osmiridium, of which there are two varieties—one sealy, consisting almost wholly of osmium, iridium, and ruthenium; while the other, which is granular, contains but mere traces of osmium and ruthenium, but is very rich in iridium and rhodium. To obtain ruthenium sealy osmiridium is heated to bright redness in a porcelain tube, through which a current of air (freed from carbonic acid by passing through potash, and from organic matter by passing through oil of vitriol), is drawn by means of an aspirator. The osmium and ruthenium are thereby oxidized, the former being carried forward as tetroxide and condensed in caustic potash solution, while the ruthenium oxide remains behind, together with iridium; and by fusing this residue with potassium hydroxide, treating the mass with water, and leaving the liquid in a corked bottle for about two hours to clarify, an orange-colored solution of potassium ruthenate is obtained, which, when neutralized with nitric acid, deposits velvet-black ruthenium sesquioxide, and this, when washed, dried, and ignited in hydrogen, yields the metal.

Ruthenium, thus prepared, forms porous lumps very much like iridium, and is moderately easy to pulverize. It is the most refractory of all metals except osmium. Deville and Debray have, however, fused it by placing it in the hottest part of the oxyhydrogen flame. After fusion it has a density of 11.4; that of the porous metal is 8.6.

Ruthenium is scarcely attacked by nitromuriatic acid. It is, however, more easily oxidized than platinum, or even than silver. When pure it is easily oxidized by fusion with potassium hydroxide, still more easily on addition of a small quantity of nitrate of chlorate, producing potassium ruthenate, which dissolves in water with orange-yellow color.

Chlorides.—Ruthenium forms three chlorides, RuCl_2 , RuCl_3 , and RuCl_4 .

The *dichloride*, RuCl_2 , is produced, together with the trichloride, by igniting pulverized ruthenium in a stream of chlorine, the trichloride then volatilizing, while the chloride remains in the form of a black crystalline powder, insoluble in water and in all acids, even nitro-muriatic acid, and only partially decomposed by alkalis. A soluble dichloride is formed by passing sulphydric acid gas into a solution of the trichloride, a brown sulphide being then precipitated, and the solution acquiring a fine blue color.

The *trichloride*, or *Ruthenium chloride*, RuCl_3 , prepared by precipitating a solution of potassic ruthenate with an acid, dissolving the precipitated black oxide in hydrochloric acid, and evaporating, is a yellow-brown, crystalline, very deliquescent mass, becoming dark-green and blue at certain points when strongly heated. It dissolves easily in water and in alcohol, leaving a small quantity of a yellow insoluble salt.

The concentrated solution of ruthenous chloride, mixed with concentrated solutions of the chlorides of potassium and ammonium, yields the double salts, $\text{RuCl}_3 \cdot 2\text{KCl}$ and $\text{RuCl}_3 \cdot 2\text{NH}_4\text{Cl}$, in the form of crystalline precipitates, with violet iridescence, very slightly soluble in water, insoluble in alcohol.

The *tetrachloride*, or *Ruthenic chloride*, RuCl_4 , is known only in its double salts. The *potassium salt*, $\text{RuCl}_4 \cdot 2\text{KCl}$, is prepared by mixing a solution of

ruthenic hydrate in hydrochloric acid with potassium chloride, and evaporating to the crystallizing point. It is brown, with rose-colored iridescence, very soluble in water, but insoluble in alcohol. The *ammonium salt*, $\text{RuCl}_3 \cdot 2\text{NH}_4\text{Cl}$, is prepared like the potassium salt, which it resembles closely.

Oxides.—Ruthenium forms five oxides, viz., RuO , Ru_2O_3 , RuO_2 , RuO_3 , and RuO_4 , the fourth, however, being known only in combination.

The *monoxide*, RuO , obtained by calcining the dichloride with sodium carbonate in a current of carbon dioxide, and washing the residue with water, has a dark-gray color and metallic lustre; is not acted upon by acids; but is reduced by hydrogen at ordinary temperatures.—The *sesquioxide*, or *Ruthenous oxide*, Ru_2O_3 , is a bluish-black powder, formed by heating the metal in the air. The corresponding hydrate, $\text{Ru}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or RuH_3O_3 , is obtained by precipitating ruthenous chloride with an alkaline carbonate, as a blackish-brown substance which dissolves with yellow color in acids.—The *dioxide*, or *Ruthenic oxide*, RuO_2 , is a black-blue powder, obtained by roasting the disulphide. *Ruthenic Hydrate*, $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ or RuH_2O_2 , is obtained as a gelatinous precipitate by decomposing potassium chlororuthenate with sodium carbonate.—The *trioxide*, RuO_3 , commonly called *ruthenic acid*, is known only as a potassium salt, which is obtained by igniting ruthenium with caustic potash and nitre; it forms an orange-yellow solution.—The *tetroxide*, RuO_4 , is a volatile compound, analogous to osmic tetroxide, obtained by heating ruthenium with potash and nitre, in a silver crucible, dissolving the fused mass in water, and passing chlorine through the solution in a tubulated retort, connected by a condensing tube with a receiver containing potash. The tetroxide then passes over and condenses in the neck of the retort and in the tube, as a golden-yellow crystalline crust, which melts between 50° and 60° . It is heavier than oil of vitriol, dissolves slightly in water, readily in hydrochloric acid, forming a solution easily decomposed by alcohol, sulphurous acid, and other reducing agents.

Sulphides.—Hydrogen sulphide, passed into a solution of either of the chlorides of ruthenium, usually forms a precipitate consisting of ruthenium sulphide and oxy-sulphide mixed with free sulphur. The blue solution of the dichloride yields a dark-brown sesquisulphide, Ru_2S_3 . When hydrogen sulphide is passed for a long time into a solution of the trichloride, ruthenium disulphide, RuS_2 , is formed, as a brown-yellow precipitate, becoming dark-brown by calcination.

Ammoniacal Ruthenium Compounds.—*Tetraammonio-hyperruthenous chloride*, $4\text{NH}_4\text{RuCl}_6 \cdot 3\text{H}_2\text{O}$ or $\text{Ru}(\text{NH}_4)_6(\text{NH}_4\text{Cl})_2 \cdot 3\text{H}_2\text{O}$, is formed by heating the solution of ammonium chlororuthenate ($\text{RuCl}_3 \cdot 2\text{NH}_4\text{Cl}$) with ammonia. It forms golden yellow oblique rhombic crystals, very soluble in water, insoluble in alcohol. Treated with silver oxide, it yields the corresponding oxide, $4\text{NH}_4\text{RuO}_4$, which, however, is decomposed by evaporation of its solution, giving off half its ammonia, and leaving the compound, $2\text{NH}_4\text{RuO}_4$. The carbonate, nitrate, and sulphate, obtained by treating this last mentioned oxide with the corresponding silver salts, form yellow crystals.

The compounds of ruthenium may readily be distinguished from those of the other platinum metals, by fusing a few milligrams of the substance on a platinum spoon, with a large excess of nitre, leaving it to cool when it becomes brittle, and dissolving the cooled mass in a little distilled water. An orange-yellow solution of potassium ruthenate is thus formed, which

on addition of a drop or two of nitric acid, yields a bulky, black precipitate; and on adding hydrochloric acid to the liquid, with the precipitate still in it, and heating it in a porcelain crucible, the oxide dissolves, forming a solution which has a fine orange-yellow color when concentrated, and when treated with *hydrogen sulphide*, till it becomes nearly black, yields a filtrate of a splendid sky-blue color. Characteristic reactions are also obtained with *potassium sulphocyanate*, which colors the liquid deep-red, changing to violet on heating, and with *lead acetate*, which forms a purple-red precipitate.

OSMIUM.

Atomic weight, 190.2 Symbol, Os.

THE separation of this metal from iridium, ruthenium, and the other metals with which it is associated in native osmiridium, and in platinum residues, depends chiefly on its ready oxidation with nitric or nitro-muriatic acid, or by ignition in air or oxygen, and the volatility of the oxide thus produced.

To prepare metallic osmium, the solution obtained by condensing the vapor of osmium tetroxide in potash (p. 455) is mixed with excess of hydrochloric acid, and digested with mercury in a well-closed bottle at 40°. The osmium is then reduced by the mercury, and an amalgam is formed, which, when distilled in a stream of hydrogen till all the mercury and calomel are expelled, leaves metallic osmium in the form of a black powder (Berzelius). The metal may also be obtained by igniting ammonium chloro-osmate with sal-ammoniac.

The properties of osmium vary according to its mode of preparation. In the pulverulent state it is black, destitute of metallic lustre, which, however, it acquires by burnishing; in the compact state, as obtained by Berzelius's method above described, it exhibits metallic lustre, and has a density of 10. Deville and Debray, by igniting precipitated osmium sulphide in a crucible of gas-cake, at the melting heat of nickel, obtained it in bluish-black, easily divisible lumps. When heated to the melting point of rhodium, it becomes more compact, and acquires a density of 21.3 to 21.4. At a still higher temperature, capable of melting ruthenium and iridium, and volatilizing platinum, osmium likewise volatilizes, but still does not melt; in fact, it is the most refractory of all metals.

Osmium in the finely-divided state is highly combustible, continuing to burn when set on fire, till it is all volatilized as tetroxide. In this state, also, it is easily oxidized by nitric or nitro-muriatic acid, being converted into tetroxide. But, after exposure to a red heat, it becomes less combustible, and is not oxidized by nitric or nitro-muriatic acid. Osmium which has been heated to the melting point of rhodium, does not give off any vapor of tetroxide when heated in the air to the melting point of zinc, but takes fire at higher temperatures.

Osmium Chlorides.—Osmium forms three chlorides, analogous to those of iridium and ruthenium. When it is heated in dry chlorine gas, there is formed, first a blue-black sublimate of the dichloride, then a red sublimate of the tetrachloride. The *dichloride*, or *hypo-osmium chloride*, dissolves in water with dark violet blue color. It is likewise formed by the action of reducing agents on either of the higher chlorides, into which, on the other hand, it is easily converted by oxidation. The addition of potas-

sium chloride renders it more stable, by forming a double salt. The *trichloride*, OsCl_3 , has not been isolated, but is contained in the solution obtained by treating the sesquioxide with hydrochloric acid. It forms double salts with alkaline chlorides. The *potassium salt*, $(\text{OsCl}_3, 3\text{KCl}, 3\text{H}_2\text{O})$, is produced, together with potassium chlorosmate, when a mixture of pulverized osmium and potassium chloride is ignited in chlorine gas; it forms dark red-brown crystals.

The *tetrachloride*, or *Osmic chloride*, OsCl_4 , is the red compound which constitutes the principal part of the product obtained by igniting osmium in chlorine gas. It dissolves with yellow color in water and alcohol, and is decomposed quickly in dilute solution, more slowly in presence of hydrochloric acid or metallic chlorides, yielding a black precipitate of osmic oxide and a solution of osmium tetroxide in hydrochloric acid.

Osmic chloride unites with the chlorides of the alkali-metals, forming salts sometimes called *osmiochlorides*, or *chlorosmates*. From the solutions of these salts, *hydrogen sulphide* and *ammonium sulphide* slowly precipitate a yellow-brown sulphide, insoluble in alkaline sulphides; *silver nitrate* forms an olive-green; *stannous chloride*, a brown precipitate. *Tannic acid*, on heating, produces a blue color, but no precipitate; *potassium ferrocyanide*, first a green, then a blue color; *potassium iodide*, a deep purple-red color. *Potash* gives a black, *ammonia* a brown precipitate, slowly in the cold, immediately on boiling. Metallic zinc and sodium formate throw down metallic osmium.

Sodium osmiochloride, $\text{OsCl}_4, 2\text{NaCl}$, prepared by heating a mixture of osmium sulphide and sodium chloride in a current of chlorine, crystallizes in orange-colored rhombic prisms, an inch long, easily soluble in water and in alcohol. The *potassium* and *ammonium salts*, of analogous composition, are obtained as red-brown crystalline precipitates on adding salt-ammoniac or potassium chloride to the solution of the sodium salt.

Oxides.—Osmium forms five oxides analogous to those of ruthenium. The *monoxide*, or *hypo-osmious oxide*, OsO , is obtained by igniting hypo-osmious sulphite in a stream of carbonic acid gas; also, as a blue-black hydrate, by heating the same salt with strong potash solution in a closed vessel. *Hypo-osmious sulphite*, OsSO_3 , or OsO, SO_2 , is a black-blue salt, produced by mixing the aqueous solution of osmium tetroxide with sulphurous acid. The *sesquioxide*, or *osmious oxide*, Os_2O_3 , is obtained by heating either of the double salts of the trichloride with sodium carbonate in a stream of carbonic acid gas. It is a black powder, insoluble in acids. The *hydrate*, obtained by precipitation, has a dirty brown-red color, is soluble in acids, but does not yield pure salts.

The *dioxide*, or *Osmic oxide*, OsO_2 , is obtained as a black insoluble powder, by heating potassium osmiochloride with sodium carbonate in a stream of carbonic acid gas, or in copper-red metallic shining lumps, by heating the corresponding hydrate. *Osmic hydrate*, $\text{OsO}_2, 2\text{H}_2\text{O}$, is obtained by precipitating a solution of potassium osmiochloride with potash, at the boiling heat, or in greater purity by mixing a solution of potassic osmite, $\text{K}_2\text{O}, \text{OsO}_3$, with dilute nitric acid.

The *trioxide*, OsO_3 , is not known in the free state, but combines with alkalis, forming salts called *osmites*, which are produced by the action of reducing agents on the tetroxide in presence of alkalis. The *potassium salt*, $\text{K}_2\text{O}, \text{OsO}_3, 2\text{H}_2\text{O}$, is a rose-colored crystalline powder.

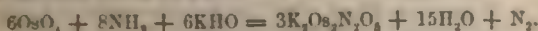
The *tetroxide*, OsO_4 , commonly called *osmic acid*, is the volatile, strong smelling compound, formed when osmium or either of its lower oxides is heated in the air, or treated with nitric or nitro-muriatic acid. It may be prepared by heating osmium in a current of oxygen gas, and condenses in the cool part of the apparatus in colorless, transparent crystals. It melts

below 100° , and boils at a temperature a little above its melting point. Its vapor has an intolerably pungent odor, attacks the eyes strongly and painfully, and is excessively poisonous. Osmium tetroxide is dissolved slowly, but in considerable quantity by water, forming an acid solution. It is a powerful oxidizing agent, decolorizing indigo-solution, separating osmium from potassium iodide, converting alcohol into aldehyde and acetic acid, etc. It dissolves in alkalis, forming yellow-red solutions, which are odorless when cold, but when heated, give off the tetroxide and free oxygen, leaving a residue of alkaline osmite.

Sulphides.—Osmium burns in sulphur vapor. Five sulphides of osmium are said to exist, analogous to the oxides, the first four being produced by decomposing the corresponding chlorides with hydrogen sulphide and the tetrasulphide by passing that gas into a solution of the tetroxide. The last is a sulphur acid, perfectly soluble in water, whereas the others are sulphur bases, slightly soluble in water, and forming deep yellow solutions.

Ammoniacal Osmium Compounds.—A cold solution of potassium osmate, mixed with sal-ammoniac, yields a yellow crystalline precipitate, consisting, according to Claus, of *hydrated osammonium chloride*, $\text{Os}(\text{NH}_3\text{Cl})_3$. An aqueous solution of the tetroxide treated with ammonia yields a brown-black powder, consisting of $\text{N}_2\text{H}_4\text{OsO}_3$, or $\text{O}=\text{Os}\begin{matrix} \text{NH}_3 \\ \diagup \quad \diagdown \\ \text{NH}_3 \end{matrix} \text{O} + \text{H}_2\text{O}$.

OSMIAMIC ACID, $\text{H}_2\text{Os}_2\text{N}_2\text{O}_5$.—The potassium salt of this bibasic acid, $\text{K}_2\text{Os}_2\text{N}_2\text{O}_5$, is produced by the action of ammonia on a hot solution of osmium tetroxide in excess of potash:—



It separates as a yellow crystalline powder, and its solution, treated with silver nitrate, yields a precipitate of silver osmiamate, $\text{Ag}_2\text{Os}_2\text{N}_2\text{O}_5$, from which the aqueous acid may be prepared by decomposition with hydrochloric acid. It is a strong acid, decomposing not only the carbonates, but also the chlorides, of potassium and sodium. The osmiamates of the alkali-metals and alkaline earth-metals are soluble in water; the lead, mercury, and silver salts are insoluble.

All osmium compounds, when heated with excess of nitric acid, give off the unpleasant odor of osmium tetroxide. By ignition in hydrogen gas, they are reduced to metallic osmium, which, as well as the lower oxide, emits the same odor when heated in contact with the air. The reactions of osmium salts in solution have already been described.

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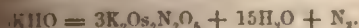
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temperature a little above its melting point. pungent odor, attacks the eyes strongly and is poisonous. Osmium tetroxide is dissolved in quantity by water, forming an acid solution. It decolorizes indigo-solution, separating indigo, converting alcohol into aldehyde and acetic acid, forming yellow-red solutions, which are, when heated, give off the tetroxide and free oxygen, leaving osmite.

It is in sulphur vapor. Five sulphides of osmium, analogous to the oxides, the first four being corresponding chlorides with hydrogen sulphide, giving that gas into a solution of the tetroxide. Osmium is soluble in water, whereas the others are insoluble in water, and forming deep yellow

Compounds.—A cold solution of potassium permanganate, yields a yellow crystalline precipitate, of hydrated osmamonium chloride, $\text{Os}(\text{NH}_4\text{Cl})_3$. Osmium tetroxide treated with ammonia yields a brown substance, $\text{N}_2\text{H}_5\text{OsO}_3$, or $\text{O}=\text{Os}\left\langle\begin{smallmatrix}\text{NH}_2 \\ \text{NH}_2\end{smallmatrix}\right\rangle\text{O} + \text{H}_2\text{O}$.

—The potassium salt of this bibasic acid, is formed by the action of ammonia on a hot solution of osmium tetroxide:—



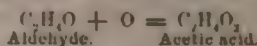
Osmium tetroxide, and its solution, treated with potassium carbonate, yields a precipitate of silver osmiamate, $\text{Ag}_2\text{Os}_2\text{N}_2\text{O}_5$, from which may be prepared by decomposition with hydrochloric acid, decomposing not only the carbonates, but also the osmium and sodium. The osmiamates of the earth-metals are soluble in water; the lead, however, is insoluble.

When heated with excess of nitric acid, give off osmium tetroxide. By ignition in hydrogen gas, osmium is reduced to osmium, which, as well as the lower oxide, is oxidized in contact with the air. The reactions have already been described.

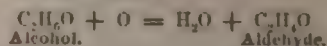
A much greater degree of regularity is observed in the effects of heat on fixed organic matters, when these are previously mixed with an excess of strong alkaline base, as potash or lime. In such cases an acid, the nature of which is chiefly dependent upon the temperature applied, is produced and remains in union with the base, the residual element or elements escaping in some volatile form. Thus benzoic acid distilled with calcium hydrate, at a dull red heat, yields calcium carbonate and benzene; woolly fibre and caustic potash, heated to a very moderate temperature, yield free hydrogen, and a brown, somewhat indefinite substance called *black acid*; with a higher degree of heat, oxalic acid appears in the place of the black acid, and, at the temperature of ignition, carbon dioxide, hydrogen being the other product.

2. *Action of Oxygen.*—Oxygen, either free or in the nascent state, in which latter condition it is most active, may act on organic compounds in four different ways:—

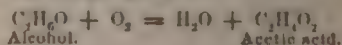
a. By simple addition, as



b. By simply removing hydrogen:



γ. By removing hydrogen and taking its place, 2 atoms of hydrogen being replaced by one of oxygen; e. g.:



δ. By removing both carbon and hydrogen. In this manner complex organic bodies containing large numbers of carbon and hydrogen atoms are reduced to others of simpler constitution, and ultimately the carbon and hydrogen are wholly converted into carbon dioxide and water. Nitrogen, chlorine, bromine, and iodine, if present, are at the same time disengaged, for the most part in the free state, and sulphur is oxidized.

Moist organic substances, especially those containing nitrogen, undergo, when exposed to the air, a slow process of oxidation, by which the organic matter is gradually burned and destroyed without sensible elevation of temperature: this process is called *Decay*, or *Erethecrosis*. Closely connected with this change are those called *Fermentation* and *Putrefaction*, consisting in a new arrangement of the elements of the compound (often with assimilation of the elements of water), and the consequent formation of new products. The change is called *putrefaction*, when it is accompanied by an offensive odor; *fermentation*, when no such odor is evolved, and especially if the change results in the formation of useful products; thus the decomposition of a dead body, or of blood or urine, is putrefaction; that of grape-juice or malt-wort, which yields alcohol, is fermentation. Putrefaction and fermentation are not processes of oxidation, nevertheless, the presence of oxygen appears to be indispensable to their commencement; but the change, when once begun, proceeds without the aid of any other substance external to the decomposing body, unless it be water or its elements. Every case of putrefaction thus begins with decay; and if the decay, or its cause, namely, the absorption of oxygen, be prevented, no putrefaction occurs. The most putrescible substances, as milk, highly azotized vegetables, and animal flesh intended for food, may be preserved indefinitely, by enclosure in metallic cases from which the air has been completely removed and excluded.

one science of chemistry, of which the study of the compounds called organic forms a part.

Organic chemistry is in fact the chemistry of carbon-compounds, and, in a strictly systematic arrangement, these compounds should be described in connection with the element carbon itself. But the compounds into which carbon enters are so numerous, their constitution and the transformations which they undergo under the influence of heat and of chemical reagents are, in many instances, so complicated, that it is found best, for the purposes of instruction, to defer their consideration till the other elements and their compounds have been studied.

It is important, in this place, to mark the distinction between organic compounds and organized bodies. Organic bodies, such as marsh gas, ethene, benzene, alcohol, sugar, morphine, etc., are definite chemical compounds, many of which, as already observed, may be formed by artificial methods; those which are solid can, for the most part, be crystallized; those which are liquid exhibit constant boiling points. Organized bodies, on the contrary, always consist of mixtures of several definite compounds. They never crystallize, but exhibit a fibrous or cellular structure, and cannot be reduced to the liquid or gaseous state without complete decomposition. Lastly, they are organs, or parts of organs, which are essentially products of vitality, and there is not the slightest prospect of their ever being produced by artificial means.

The study of the composition and chemical relations of organized bodies belongs to a special department of the science called "Physiological Chemistry," which bears the same relation to Organic Chemistry that Chemical Geology bears to Mineralogy.

DECOMPOSITIONS AND TRANSFORMATIONS OF ORGANIC COMPOUNDS.

Organic bodies are, generally speaking, distinguished by the facility with which they decompose under the influence of heat or of chemical reagents; the more complex the body, the more easily does it undergo decomposition or transformation.

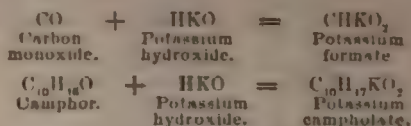
1. *Action of Heat.*—Organic bodies of simple constitution and of some permanence, but not capable of subliming unchanged, like many of the organic acids, yield, when exposed to a high but regulated temperature, in a retort, new compounds, perfectly definite and often crystallizable, which partake, to a certain extent, of the properties of the original substance. Carbon dioxide and water are often eliminated under these circumstances. If the heat be suddenly raised to redness, the regularity of the decomposition vanishes, while the products become more uncertain and more numerous; carbon dioxide and watery vapor are succeeded by inflammable gases, as carbon monoxide and hydrocarbons; oily matter and tar distil over, and increase in quantity until the close of the operation, when the retort is found to contain, in most cases, a residue of charcoal. Such is *dry or destructive distillation*.

If the organic substance contains nitrogen, and it is not of a kind capable of taking a new and permanent form at a moderate degree of heat, then that nitrogen is in most instances partly disengaged in the shape of ammonia, or substances analogous to it, partly left in combination with the carbonaceous matter in the distillatory vessel. The products of dry distillation thus become still more complicated.

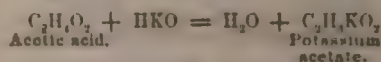
This action takes place most readily with the strongest nitric acid (pure hydrogen nitrate). The products (called *nitro-compounds*) are always easily combustible, and in many cases highly explosive.

5. *Action of Alkalies*.—The hydroxides of potassium and sodium act on organic bodies in a great variety of ways, the most important and general of which are the following:—

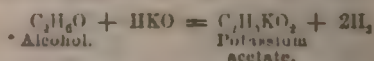
a. By direct combination:—



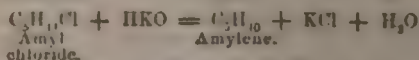
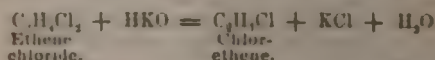
b. By double decomposition with acids, water being eliminated, and a salt produced:



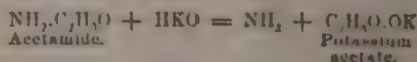
γ. Oxidation, with elimination of hydrogen:



δ. From chlorinated compounds they remove a part or the whole of the chlorine:



ε. Amides (p. 318) are decomposed by them in such a manner that the whole of the nitrogen is given off as ammonia, and a potassium or sodium salt of the corresponding acid is produced:



Many other azotized organic compounds, when heated with alkaline hydroxides, likewise give up the whole of their hydrogen in the form of ammonia.

6. *Action of Reducing Agents*.—This name is given to bodies whose action is the inverse of that of oxygen, chlorine, bromine, and iodine, such are nascent hydrogen, obtained by the action of sodium-amalgam on water, or by that of zinc on aqueous acids or alkalies, also hydrogen sulphide, ammonium sulphide, sulphurous acid, and metals, especially potassium and sodium—all of which either give up hydrogen, or abstract oxygen, chlorine, etc.

Reducing agents may act in the following ways:—

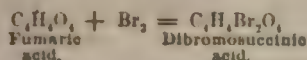
a. By adding hydrogen to an organic body:—



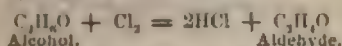
Fermentation and putrefaction are always accompanied by the development of certain living organisms of the fungous class; but whether the growth of these is a cause or a consequence of the chemical change is a point not yet decided. We shall return to this subject in speaking of the fermentation of sugar.

3. *Action of Chlorine, Bromine, and Iodine.*—Chlorine and bromine exert precisely similar actions on organic bodies; that of chlorine is the more energetic of the two. The reactions consist:

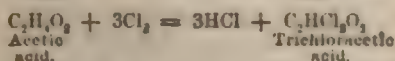
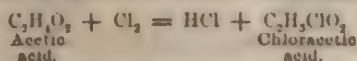
4. In simple addition of chlorine or bromine to the organic molecule; e.g.:



5. In removal of hydrogen without substitution:



6. In substitution of chlorine or bromine for hydrogen:



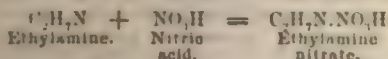
The substitution-products thus formed undergo transformations closely analogous to those of the original compounds, under the influence of similar reagents; but they are always more acid, or less basylous, in proportion to the quantity of chlorine or bromine substituted for hydrogen. Thus aniline, $\text{C}_6\text{H}_7\text{N}$, which is a strong base, may be converted, by processes to be hereafter described, into the chlorinated compounds, $\text{C}_6\text{H}_6\text{ClN}$, $\text{C}_6\text{H}_5\text{Cl}_2\text{N}$, and $\text{C}_6\text{H}_4\text{Cl}_3\text{N}$, the first and second of which are less basic than aniline itself, while the third does not show any tendency to form salts with acids.

7. In presence of water they remove the hydrogen of that liquid, and set free the oxygen: hence, chlorine-water and bromine-water act as powerful oxidizing agents.

Iodine may also act in this manner as an oxidizing agent; and it sometimes attaches itself directly to organic molecules; but it never acts directly by substitution. Iodine substitution-products may, however, be obtained in some cases by treating organic bodies with chloride of iodine, the chlorine then removing hydrogen, and the iodine taking its place.

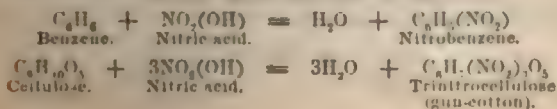
4. *Action of Nitric Acid.*—This acid acts very powerfully on organic substances. The action may be of three kinds:

a. Direct combination, as with organic bases; e.g.:



5. Oxidation. This mode of action is most frequently observed with the somewhat diluted acid.

6. Substitution of nitryl (NO_2) for hydrogen; e.g.:



complexity of structure, in consequence of the accumulation of a large number of carbon atoms in the same molecule.

Determination of Carbon and Hydrogen.—The quantities of these elements are determined by heating a known weight of the body to be analyzed in contact with some easily reducible metallic oxide, black oxide of copper being the substance generally used. The organic body then undergoes complete combustion at the expense of the oxygen of the copper oxide, the carbon being converted into carbon dioxide, and the hydrogen into water. These products are collected and their weights determined, and from the data thus obtained the quantities of carbon and hydrogen present in the organic substance are calculated. When nothing but carbon and hydrogen, or these bodies together with oxygen, is present, one experiment suffices; the carbon and hydrogen are determined directly, and the oxygen by difference.

The substance to be analyzed, if solid, must be carefully freed from moisture. If it will bear the application of a moderate heat, this deaeration is very easily accomplished by a water- or steam-bath; in other cases, exposure at common temperatures to the absorbent powers of a large surface of oil of vitriol in the vacuum of an air-pump must be substituted.

The copper oxide is best made from the nitrate by complete ignition in an earthen crucible; it is reduced to powder and reheated just before use, to expel hygroscopic moisture, which it absorbs with avidity, even while warm. The combustion is performed in a tube of hard white Bohemian glass, having a diameter of 0.4 or 0.5 inch, and varying in length from 14 to 18 inches: this kind of glass bears a moderate red heat without becoming soft enough to lose its shape. One end of the tube is drawn out to a point as shown in fig. 160, and closed; the other is simply heated to fuse and

Fig. 160.

Copper oxide. Mixture. Copper oxide.



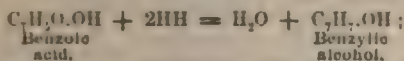
soften the sharp edges of the glass. To prevent absorption of moisture by the copper oxide during the filling of the tube, the oxide, while still hot, is poured into a long-necked flask closed by a cork; it is then left to cool, and afterwards mixed with the organic substance in the combustion-tube itself. A small quantity of the cooled oxide is first introduced into the tube, then a portion of the organic substance is added, and upon this a column of oxide about 3 inches long is poured in the same manner as before. This portion of oxide is mixed with the organic substance by stirring it with a clean iron rod, the extremity of which is bent into two turns of a screw; and when it is thoroughly incorporated, the rest of the substance is introduced, then another column of oxide of the same length as before, and the stirring is repeated. Lastly, the rest of the tube is filled with pure oxide.

The tube is then ready to be placed in the furnace or chauffer: that, when charcoal is the fuel employed, is constructed of thin sheet iron, and is furnished with a series of supports of equal height, which serve to prevent flexure of the combustion tube when softened by heat. The chauffer is placed upon flat bricks or a piece of stone, so that but little air can enter the grating, unless the whole be purposely raised. A slight inclination is also given towards the extremity occupied by the mouth of the combustion-tube, which passes through a hole provided for that purpose.

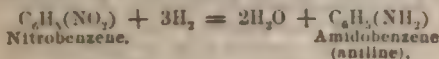
6. By removing oxygen, chlorine, bromine, or iodine, without introducing anything in its place; thus:—



7. By substituting hydrogen for oxygen, chlorine, etc. This process is called *inverse substitution*. It may take place either in equivalent quantities, e. g.:—

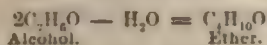
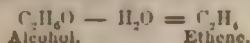


or it may happen that the quantity of hydrogen introduced is only half that which is equivalent to the oxygen removed. This mode of substitution takes place with nitro-compounds, which are thereby reduced to others containing amidogen (NH_2) in place of nitryl (NO_2); thus:—



A large number of organic bases are formed in this manner from nitro-compounds.

7. *Action of Dehydrating Agents.*—Strong sulphuric acid, sulphuric oxide, phosphoric oxide, and zinc chloride, remove oxygen and hydrogen from organic bodies in the form of water, the elements of which are derived, sometimes from a single molecule of the organic body, sometimes from two molecules:—



Compounds which, like sugar, starch, and woody fibre, consist of carbon united with hydrogen and oxygen in the proportions to form water, are often reduced by these dehydrating agents to black substances consisting mainly of carbon.

Other reactions of less generality than those above described will be sufficiently illustrated by special cases in the sequel.

THE ELEMENTARY OR ULTIMATE ANALYSIS OF ORGANIC COMPOUNDS.

Organic compounds contain, for the most part, only a small number of elements. Many consist only of carbon and hydrogen. A very large number, including most of those which occur ready-formed in the bodies of plants and animals, consist of carbon, hydrogen and oxygen; others consist of carbon, hydrogen, and nitrogen. Others, again, including most of the proximate principles of the animal organism, consist of four elements, carbon, hydrogen, oxygen, and nitrogen. Some contain sulphur, phosphorus, chlorine, and metallic elements; in fact, artificially prepared carbon compounds may contain any elements whatever. Moreover, even those which contain only a small number of elements often exhibit great

ruthenic hydrate in hydrochloric acid with potassium chloride, and evaporating to the crystallizing point. It is brown, with rose-colored iridescence, very soluble in water, but insoluble in alcohol. The ammonium salt, $\text{RuCl}_2 \cdot 2\text{NH}_4\text{Cl}$, is prepared like the potassium salt, which it resembles closely.

Oxides.—Ruthenium forms five oxides, viz., RuO , Ru_2O_3 , RuO_2 , RuO_3 , and RuO_4 , the fourth, however, being known only in combination.

The monoxide, RuO , obtained by calcining the dichloride with sodium carbonate in a current of carbon dioxide, and washing the residue with water, has a dark-gray color and metallic lustre; is not acted upon by acids; but is reduced by hydrogen at ordinary temperatures.—The sesquioxide, or Ruthenous oxide, Ru_2O_3 , is a bluish-black powder, formed by heating the metal in the air. The corresponding hydrate, $\text{Ru}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, or RuH_2O_3 , is obtained by precipitating ruthenous chloride with an alkaline carbonate, as a blackish-brown substance which dissolves with yellow color in acids.—The dioxide, or Ruthenic oxide, RuO_2 , is a black-blue powder, obtained by roasting the disulphide. Ruthenic Hydrate, $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ or RuH_2O_2 , is obtained as a gelatinous precipitate by decomposing potassium chlororuthenate with sodium carbonate.—The trioxide, RuO_3 , commonly called ruthenic acid, is known only as a potassium salt, which is obtained by igniting ruthenium with caustic potash and nitre: it forms an orange-yellow solution.—The tetroxide, RuO_4 , is a volatile compound, analogous to osmic tetroxide, obtained by heating ruthenium with potash and nitre, in a silver crucible, dissolving the fused mass in water, and passing chlorine through the solution in a tubulated retort, connected by a condensing tube with a receiver containing potash. The tetroxide then passes over and condenses in the neck of the retort and in the tube, as a golden-yellow crystalline crust, which melts between 50° and 60° . It is heavier than oil of vitriol, dissolves slightly in water, readily in hydrochloric acid, forming a solution easily decomposed by alcohol, sulphurous acid, and other reducing agents.

Sulphides.—Hydrogen sulphide, passed into a solution of either of the chlorides of ruthenium, usually forms a precipitate consisting of ruthenium sulphide and oxysulphide mixed with free sulphur. The blue solution of the dichloride yields a dark-brown sesquisulphide, Ru_2S_3 . When hydrogen sulphide is passed for a long time into a solution of the trichloride, ruthenium disulphide, RuS_2 , is formed, as a brown-yellow precipitate, becoming dark-brown by calcination.

Ammoniacal Ruthenium Compounds.—Tetrammonio-hyporuthenious Chloride, $4\text{NH}_4 \cdot \text{RuCl}_2 \cdot 3\text{H}_2\text{O}$, or $\text{Ru}[\text{NH}_2(\text{NH}_4)\text{Cl}]_2 \cdot 3\text{H}_2\text{O}$, is formed by boiling the solution of ammonium chlororuthenate ($\text{RuCl}_2 \cdot 2\text{NH}_4\text{Cl}$) with ammonia. It forms golden-yellow oblique rhombic crystals, very soluble in water, insoluble in alcohol. Treated with silver oxide, it yields the corresponding oxide, $4\text{NH}_3 \cdot \text{RuO}$, which, however, is decomposed by evaporation of its solution, giving off half its ammonia, and leaving the compound, $2\text{NH}_3 \cdot \text{RuO}$. The carbonate, nitrate, and sulphate, obtained by treating this last-mentioned oxide with the corresponding silver salts, form yellow crystals.

The compounds of ruthenium may readily be distinguished from those of the other platinum-metals, by fusing a few milligrams of the substance in a platinum spoon, with a large excess of nitre, leaving it to cool when it ceases to froth, and dissolving the cooled mass in a little distilled water. An orange-yellow solution of potassium ruthenate is thus formed, which

on addition of a drop or two of nitric acid, yields a bulky, black precipitate, and on adding hydrochloric acid to the liquid, with the precipitate still in it, and heating it in a porcelain crucible, the oxide dissolves, forming a solution which has a fine orange-yellow color when concentrated, and when treated with *hydrogen sulphide*, till it becomes nearly black, yields a filtrate of a splendid sky-blue color. Characteristic reactions are also obtained with *potassium sulphocyanate*, which colors the liquid deep-red, changing to violet on heating, and with *lead acetate*, which forms a purple-red precipitate.

OSMIUM.

Atomic weight, 190.2 Symbol, Os.

The separation of this metal from iridium, ruthenium, and the other metals with which it is associated in native osmiridium, and in platinum residues, depends chiefly on its ready oxidation with nitric or nitro-muriatic acid, or by ignition in air or oxygen, and the volatility of the oxide thus produced.

To prepare metallic osmium, the solution obtained by condensing the vapor of osmium tetroxide in potash (p. 455) is mixed with excess of hydrochloric acid, and digested with mercury in a well-closed bottle at 40°. The osmium is then reduced by the mercury, and an amalgam is formed, which, when distilled in a stream of hydrogen till all the mercury and calomel are expelled, leaves metallic osmium in the form of a black powder (Berzelius). The metal may also be obtained by igniting ammonium chloro-osmiate with sal-ammoniac.

The properties of osmium vary according to its mode of preparation. In the pulverulent state it is black, destitute of metallic lustre, which, however, it acquires by burnishing; in the compact state, as obtained by Berzelius's method above described, it exhibits metallic lustre, and has a density of 10. Deville and Debray, by igniting precipitated osmium sulphide in a crucible of gas-coke, at the melting heat of nickel, obtained it in bluish-black, easily divisible lumps. When heated to the melting point of rhodium, it becomes more compact, and acquires a density of 21.3 to 21.4. At a still higher temperature, capable of melting ruthenium and rhodium, and volatilizing platinum, osmium likewise volatilizes, but still does not melt; in fact, it is the most refractory of all metals.

Osmium in the finely divided state is highly combustible, continuing to burn when set on fire, till it is all volatilized as tetroxide. In this state, also, it is easily oxidized by nitric or nitro-muriatic acid, being converted into tetroxide. But, after exposure to a red heat, it becomes less combustible, and is not oxidized by nitric or nitro-muriatic acid. Osmium which has been heated to the melting point of rhodium, does not give off any vapor of tetroxide when heated in the air to the melting point of zinc, but takes fire at higher temperatures.

Osmium Chlorides.—Osmium forms three chlorides, analogous to those of iridium and ruthenium. When it is heated in dry chlorine gas, there is formed, first a blue-black sublimate of the dichloride, then a red sublimate of the tetrachloride. The dichloride, or *hypo-osmium chloride*, dissolves in water with dark violet blue color. It is likewise formed by the action of reducing agents on either of the higher chlorides, into which, on the other hand, it is easily converted by oxidation. The addition of potas-

acids: but is reduced by hydrogen at ordinary temperatures.—The *oxide*, or *Ruthenious oxide*, Ru_2O_3 , is a bluish-black powder, formed by igniting the metal in the air. The corresponding hydrate, $\text{Ru}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is obtained by precipitating ruthenious chloride with an alkali carbonate, as a blackish-brown substance which dissolves with color in acids.—The *dioxide*, or *Ruthenic oxide*, RuO_2 , is a black-black powder, obtained by roasting the disulphide. *Ruthenic Hydrate*, $\text{RuO}_2 \cdot \text{H}_2\text{O}$ or RuH_2O_4 , is obtained as a gelatinous precipitate by decomposing sodium chlororuthenate with sodium carbonate.—The *trioxide*, RuO_3 , commonly called *ruthenic acid*, is known only as a potassium salt, was obtained by igniting ruthenium with caustic potash and nitre: it is in an orange-yellow solution.—The *tetroxide*, RuO_4 , is a volatile compound analogous to osmic tetroxide, obtained by heating ruthenium with nitre, in a silver crucible, dissolving the fused mass in water, passing chlorine through the solution in a tubulated retort, connected with a condensing tube with a receiver containing potash. The tetroxide passes over and condenses in the neck of the retort and in the tail, forming a golden-yellow crystalline crust, which melts between 50° and 60° , is heavier than oil of vitriol, dissolves slightly in water, readily in chloric acid, forming a solution easily decomposed by alcohol, sulphuric acid, and other reducing agents.

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liquefaction. A proper quantity of the substance to be analyzed, namely, from 5 to 10 grains, is dried and accurately weighed out : this is mixed in a warm porcelain mortar with enough of the soda-lime to fill two-thirds of an ordinary combustion-tube, the mortar being rinsed with a little more of the alkaline mixture, and, lastly, with a small quantity of powdered glass, which completely removes everything adherent to its surface; the tube is then filled to within an inch of the open end with the lime-mixture, and arranged in the chaffier in the usual manner. The ammonia is collected in a little apparatus of three bulbs (fig. 170), containing mole-

Fig. 170.



ately strong hydrochloric acid, attached by a cork to the combustion-tube. Matters being thus adjusted, fire is applied to the tube, commencing with the interior extremity. When it is ignited throughout its whole length, and when no gas issues from the apparatus, the point of the tube is broken, and a little air drawn through the whole. The acid liquid is then emptied into a capsule, the bulbs rinsed into the same, first with a little alcohol, and then repeatedly with distilled water; an excess of pure platonic chloride is added; and the whole evaporated to dryness in a water-bath. The dry mass, when cold, is treated with a mixture of alcohol and ether, which dissolves out the superfluous platinum chloride, but leaves untouched the yellow crystalline ammonium platinochloride. The latter is collected upon a small weighed filter, washed with the same mixture of alcohol and ether, dried at 100° , and weighed; 100 parts correspond to 6.272 parts of nitrogen. Or, the salt with its filter may be very carefully ignited, the filter burned in a platinum crucible, and the nitrogen reckoned from the weight of the spongy metal, 100 parts of that substance being equivalent to 14.18 parts of nitrogen. The former plan is to be preferred in most cases.

Bodies very rich in nitrogen, as urea, must be mixed with about an equal quantity of pure sugar, to furnish uncondensable gas, and thus diminish the violence of the absorption which otherwise occurs, and the same precaution must be taken, for a different reason, with those which contain little or no hydrogen.

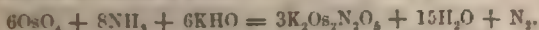
A modification of this process has been suggested by Peligot, which is very convenient if a large number of nitrogen-determinations is to be made. By this plan, the ammonia, instead of being received in hydrochloric acid, is conducted into a known volume ($\frac{1}{4}$ to 1 cubic inch) of a standard solution of sulphuric acid contained in the ordinary nitrogen-bulbs. After the combustion is finished, the acid containing the ammonia is poured out into a beaker, colored with a drop of tincture of litmus, and then neutralized with a standard solution of soda in water, or of lime in sugar-water, the point of neutralization becoming perceptible by the sudden appearance of a blue tint. The lime-solution is conveniently poured out from an alkalmeter. The volume of lime-solution necessary to neutralize the same amount of acid that is used for condensing the ammonia, having been ascertained by a preliminary experiment, it is evident that the difference of the quantities used in the two experiments gives the ammonia

below 100° , and boils at a temperature a little above its melting point. Its vapor has an intolerably pungent odor, attacks the eyes strongly and painfully, and is excessively poisonous. Osmium tetroxide is dissolved slowly, but in considerable quantity by water, forming an acid solution. It is a powerful oxidizing agent, decolorizing indigo-solution, separating iodine from potassium iodide, converting alcohol into aldehyde and acetic acid, etc. It dissolves in alkalis, forming yellow-red solutions, which are colorless when cold, but when heated, give off the tetroxide and free oxygen, leaving a residue of alkaline osmite.

Sulphides.—Osmium burns in sulphur vapor. Five sulphides of osmium are said to exist, analogous to the oxides, the first four being produced by decomposing the corresponding chlorides with hydrogen sulphide and the tetrasulphide by passing that gas into a solution of the tetroxide. The last is a sulphur acid, perfectly soluble in water, whereas the others are sulphur bases, slightly soluble in water, and forming deep yellow solutions.

Ammoniacal Osmium Compounds.—A cold solution of potassium osmate, mixed with sal-ammoniac, yields a yellow crystalline precipitate, consisting, according to Claus, of *hydrated osmium ammonium chloride*, $\text{Os}(\text{NH}_4\text{Cl})_2$. An aqueous solution of the tetroxide treated with ammonia yields a brown-black powder, consisting of $\text{N}_2\text{H}_4\text{OsO}_3$, or $\text{O}=\text{Os}\left\langle\begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}\right\rangle\text{O} + \text{H}_2\text{O}$.

Osmiamic Acid, $\text{H}_2\text{Os}_2\text{N}_2\text{O}_6$.—The potassium salt of this bibasic acid, $\text{K}_2\text{Os}_2\text{N}_2\text{O}_6$, is produced by the action of ammonia on a hot solution of osmium tetroxide in excess of potash:—



It separates as a yellow crystalline powder, and its solution, treated with silver nitrate, yields a precipitate of silver osmiamate, $\text{Ag}_2\text{Os}_2\text{N}_2\text{O}_6$, from which the aqueous acid may be prepared by decomposition with hydrochloric acid. It is a strong acid, decomposing not only the carbonates, but also the chlorides, of potassium and sodium. The osmiamates of the alkali-metals and alkaline earth-metals are soluble in water; the lead, mercury, and silver salts are insoluble.

All osmium compounds, when heated with excess of nitric acid, give off the unpleasant odor of osmium tetroxide. By ignition in hydrogen gas, they are reduced to metallic osmium, which, as well as the lower oxide, emits the same odor when heated in contact with the air. The reactions of osmium salts in solution have already been described.

PART III.

CHEMISTRY OF CARBON COMPOUNDS

OR

ORGANIC CHEMISTRY.

INTRODUCTION.

THE term "Organic Chemistry" originally denoted the chemistry of compounds formed in the bodies of plants and animals. The peculiar characters of the compounds thus formed, and the failure of the earlier attempts to produce them by artificial means, led to the erroneous idea that their formation was due to a mysterious power, called "vital force," supposed to reside in the living organism, and to govern all the changes and processes taking place within it. In accordance with this idea, the chemistry of organic compounds, including those which were formed by artificial processes from the products of vegetable and animal life, was erected into a special branch of chemical science.

Later researches have, however, shown that a large number of compounds, formerly regarded as producible only under the influence of the so-called vital force, may be formed either by direct combination of their elements, or by chemical transformation of inorganic compounds.

The first step in the formation of organic compounds from their elements was made by Wöhler, who showed, in 1828, that urea, the characteristic constituent of urine, can be produced by molecular transformation of ammonium cyanate. This experiment, viewed in connection with the fact established about twelve years afterwards, that cyanogen (CN) can be formed by direct combination of its elements, is conclusive of the possibility of forming a product of the living organism from inorganic materials. More recently it has been shown that ethine, or acetylene, C_2H_2 , can be produced by the direct combination of carbon and hydrogen; that this compound can be made to take up two additional atoms of hydrogen to form ethene, C_2H_4 ; and that this latter compound can be converted into alcohol, C_2H_5O , a body formerly supposed to be producible only by the fermentation of sugar; and from this a large number of other compounds can be produced by the action of various reagents. The researches of Berthollet, Kolbe, Wurtz, and other distinguished chemists, have led to the discovery of a large number of other cases of the formation of organic compounds, often of great complexity, from substances of purely mineral origin, and ultimately from the elements themselves. The division of compounds into two distinct branches, inorganic and organic—formed according to distinct laws, the former being artificially producible by direct combination of their elements, the latter only under the influence of a supposed vital force—must therefore be abandoned. There is, indeed, but

one science of chemistry, of which the study of the compounds called organic forms a part.

Organic chemistry is in fact the chemistry of carbon-compounds, and, in a strictly systematic arrangement, these compounds should be described in connection with the element carbon itself. But the compounds into which carbon enters are so numerous, their constitution and the transformations which they undergo under the influence of heat and of chemical reagents are, in many instances, so complicated, that it is found best, for the purposes of instruction, to defer their consideration till the other elements and their compounds have been studied.

It is important, in this place, to mark the distinction between organic compounds and organized bodies. Organic bodies, such as marsh gas, ethene, benzene, alcohol, sugar, morphine, etc., are definite chemical compounds, many of which, as already observed, may be formed by artificial methods; those which are solid can, for the most part, be crystallized; those which are liquid exhibit constant boiling points. Organized bodies, on the contrary, always consist of mixtures of several definite compounds. They never crystallize, but exhibit a fibrous or cellular structure, and cannot be reduced to the liquid or gaseous state without complete decomposition. Lastly, they are organs, or parts of organs, which are essentially products of vitality, and there is not the slightest prospect of their ever being produced by artificial means.

The study of the composition and chemical relations of organized bodies belongs to a special department of the science called "Physiological Chemistry," which bears the same relation to Organic Chemistry that Chemical Geology bears to Mineralogy.

DECOMPOSITIONS AND TRANSFORMATIONS OF ORGANIC COMPOUNDS.

Organic bodies are, generally speaking, distinguished by the facility with which they decompose under the influence of heat or of chemical reagents: the more complex the body, the more easily does it undergo decomposition or transformation.

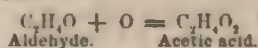
1 *Action of Heat.*—Organic bodies of simple constitution and of some permanence, but not capable of subliming unchanged, like many of the organic acids, yield, when exposed to a high but regulated temperature, in a retort, new compounds, perfectly definite and often crystallizable, which partake, to a certain extent, of the properties of the original substance. Carbon dioxide and water are often eliminated under these circumstances. If the heat be suddenly raised to redness, the regularity of the decomposition vanishes, while the products become more uncertain and more numerous; carbon dioxide and watery vapor are succeeded by inflammable gases, as carbon monoxide and hydrocarbons; oily matter and tar distil over, and increase in quantity until the close of the operation, when the retort is found to contain, in most cases, a residue of charcoal. Such is *dry or destructive distillation*.

If the organic substance contains nitrogen, and it is not of a kind capable of taking a new and permanent form at a moderate degree of heat, then that nitrogen is in most instances partly disengaged in the shape of ammonia, or substances analogous to it, partly left in combination with the carbonaceous matter in the distillatory vessel. The products of dry distillation thus become still more complicated.

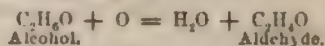
A much greater degree of regularity is observed in the effects of heat on fixed organic matters, when these are previously mixed with an excess of strong alkaline base, as potash or lime. In such cases an acid, the nature of which is chiefly dependent upon the temperature applied, is produced, and remains in union with the base, the residual element or elements escaping in some volatile form. Thus benzoic acid distilled with calcium hydrate, at a dull red heat, yields calcium carbonate and benzene; woolly fibre and caustic potash, heated to a very moderate temperature, yield free hydrogen, and a brown, somewhat indefinite substance called *alum acid*; with a higher degree of heat, oxalic acid appears in the place of the alum; and, at the temperature of ignition, carbon dioxide, hydrogen being the other product.

2. *Action of Oxygen*.—Oxygen, either free or in the nascent state, in which latter condition it is most active, may act on organic compounds in four different ways:—

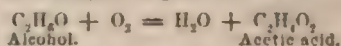
a. By simple addition, as



b. By simply removing hydrogen:



γ. By removing hydrogen and taking its place, 2 atoms of hydrogen being replaced by one of oxygen; e. g.:



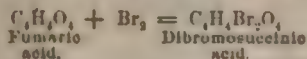
3. By removing both carbon and hydrogen. In this manner complex organic bodies containing large numbers of carbon and hydrogen atoms are reduced to others of simpler constitution, and ultimately the carbon and hydrogen are wholly converted into carbon dioxide and water. Nitrogen, chlorine, bromine, and iodine, if present, are at the same time disengaged, for the most part in the free state, and sulphur is oxidized.

Moist organic substances, especially those containing nitrogen, undergo, when exposed to the air, a slow process of oxidation, by which the organic matter is gradually burned and destroyed without sensible elevation of temperature: this process is called *Decay*, or *Erethismia*. Closely connected with this change are those called *Fermentation* and *Putrefaction*, consisting in a new arrangement of the elements of the compound (often with assimilation of the elements of water), and the consequent formation of new products. The change is called *putrefaction*, when it is accompanied by an offensive odor; *fermentation*, when no such odor is evolved, and especially if the change results in the formation of useful products, thus the decomposition of a dead body, or of blood or urine, is putrefaction; that of grape-juice or malt-wort, which yields alcohol, is fermentation. Putrefaction and fermentation are not processes of oxidation; nevertheless, the presence of oxygen appears to be indispensable to their commencement; but the change, when once begun, proceeds without the aid of any other substance external to the decomposing body, unless it be water or its elements. Every case of putrefaction thus begins with decay; and if the decay, or its cause, namely, the absorption of oxygen, be prevented, no putrefaction occurs. The most putrescible substances, as milk, highly azotized vegetables, and animal flesh intended for food, may be preserved indefinitely, by inclosure in metallic cases from which the air has been completely removed and excluded.

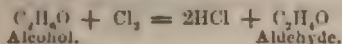
Fermentation and putrefaction are always accompanied by the development of certain living organisms of the fungous class; but whether the growth of these is a cause or a consequence of the chemical change is a point not yet decided. We shall return to this subject in speaking of the fermentation of sugar.

3. *Action of Chlorine, Bromine, and Iodine.*—Chlorine and bromine exert precisely similar actions on organic bodies; that of chlorine is the more energetic of the two. The reactions consist:

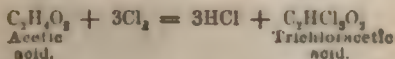
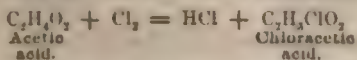
a. In simple addition of chlorine or bromine to the organic molecule; e.g.:



b. In removal of hydrogen without substitution:



γ. In substitution of chlorine or bromine for hydrogen:



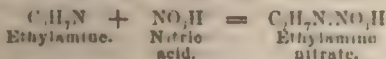
The substitution-products thus formed undergo transformations closely analogous to those of the original compounds, under the influence of similar reagents; but they are always more acid, or less basyous, in proportion to the quantity of chlorine or bromine substituted for hydrogen. Thus aniline, $\text{C}_6\text{H}_7\text{N}$, which is a strong base, may be converted, by processes to be hereafter described, into the chlorinated compounds, $\text{C}_6\text{H}_6\text{ClN}$, $\text{C}_6\text{H}_5\text{Cl}_2\text{N}$, and $\text{C}_6\text{H}_4\text{Cl}_3\text{N}$, the first and second of which are less basic than aniline itself, while the third does not show any tendency to form salts with acids.

b. In presence of water they remove the hydrogen of that liquid, and set free the oxygen: hence, chlorine-water and bromine-water act as powerful oxidizing agents.

Iodine may also act in this manner as an oxidizing agent; and it sometimes attaches itself directly to organic molecules; but it never acts directly by substitution. Iodine substitution-products may, however, be obtained in some cases by treating organic bodies with chloride of iodine, the chlorine then removing hydrogen, and the iodine taking its place.

4. *Action of Nitric Acid.*—This acid acts very powerfully on organic substances. The action may be of three kinds:

a. Direct combination, as with organic bases; e.g.:



b. Oxidation. This mode of action is most frequently observed with the somewhat diluted acid.

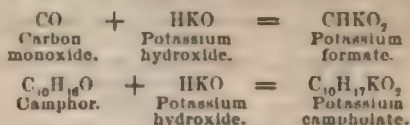
γ. Substitution of nityl (NO_2) for hydrogen; e.g.:



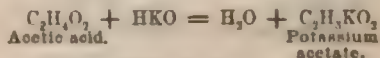
This action takes place most readily with the strongest nitric acid (pure hydrogen nitrate). The products (called nitro-compounds) are always easily combustible, and in many cases highly explosive.

5. *Action of Alkalies.*—The hydroxides of potassium and sodium act on organic bodies in a great variety of ways, the most important and general of which are the following:—

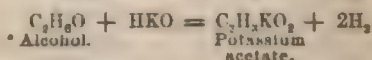
a. By direct combination:—



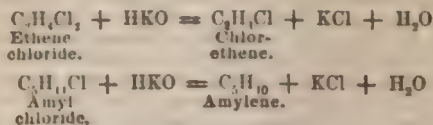
b. By double decomposition with acids, water being eliminated, and a salt produced:



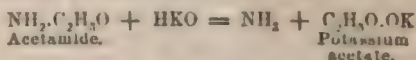
γ. Oxidation, with elimination of hydrogen:



δ. From chlorinated compounds they remove a part or the whole of the chlorine:



e. Amides (p. 318) are decomposed by them in such a manner that the whole of the nitrogen is given off as ammonia, and a potassium or sodium salt of the corresponding acid is produced:

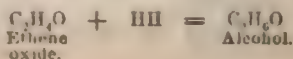


Many other azotized organic compounds, when heated with alkaline hydroxides, likewise give up the whole of their hydrogen in the form of ammonia.

6. *Action of Reducing Agents.*—This name is given to bodies whose action is the inverse of that of oxygen, chlorine, bromine, and iodine; such are nascent hydrogen, obtained by the action of sodium-amalgam on water, or by that of zinc on aqueous acids or alkalies; also hydrogen sulphide, ammonium sulphide, sulphurous acid, and metals, especially potassium and sodium—all of which either give up hydrogen, or abstract oxygen, chlorine, etc.

Reducing agents may act in the following ways:—

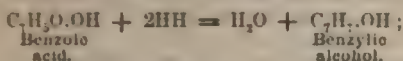
a. By adding hydrogen to an organic body:—



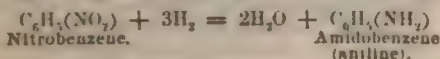
6. By removing oxygen, chlorine, bromine, or iodine, without introducing anything in its place; thus:—



7. By substituting hydrogen for oxygen, chlorine, etc. This process is called *inverse substitution*. It may take place either in equivalent quantities, e.g.:—

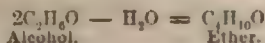
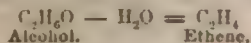


or it may happen that the quantity of hydrogen introduced is only half that which is equivalent to the oxygen removed. This mode of substitution takes place with nitro-compounds, which are thereby reduced to others containing amidogen (NH_2) in place of nityl (NO_2); thus:—



A large number of organic bases are formed in this manner from nitro-compounds.

7. *Action of Dehydrating Agents.*—Strong sulphuric acid, sulphuric oxide, phosphoric oxide, and zinc chloride, remove oxygen and hydrogen from organic bodies in the form of water, the elements of which are derived, sometimes from a single molecule of the organic body, sometimes from two molecules:—



Compounds which, like sugar, starch, and woody fibre, consist of carbon united with hydrogen and oxygen in the proportions to form water, are often reduced by these dehydrating agents to black substances consisting mainly of carbon.

Other reactions of less generality than those above described will be sufficiently illustrated by special cases in the sequel.

THE ELEMENTARY OR ULTIMATE ANALYSIS OF ORGANIC COMPOUNDS.

Organic compounds contain, for the most part, only a small number of elements. Many consist only of carbon and hydrogen. A very large number, including most of those which occur ready-formed in the bodies of plants and animals, consist of carbon, hydrogen and oxygen; others consist of carbon, hydrogen, and nitrogen. Others, again, including most of the proximate principles of the animal organism, consist of four elements, carbon, hydrogen, oxygen, and nitrogen. Some contain sulphur, phosphorus, chlorine, and metallic elements; in fact, artificially prepared carbon compounds may contain any elements whatever. Moreover, even those which contain only a small number of elements often exhibit great

sent in the organic substance are calculated. When nothing is and hydrogen, or those bodies together with oxygen, is present, oxygen suffices; the carbon and hydrogen are determined direct the oxygen by difference.

The substance to be analyzed, if solid, must be carefully freed from moisture. If it will bear the application of a moderate heat, the operation is very easily accomplished by a water- or steam-bath: in other cases, exposure at common temperatures to the absorbent powers of a surface of oil of vitriol in the vacuum of an air-pump must be substituted.

The copper oxide is best made from the nitrate by complete ignition in an earthen crucible; it is reduced to powder and reheated just below red heat to expel hygroscopic moisture, which it absorbs with avidity, even when warm. The combustion is performed in a tube of hard white glass, having a diameter of 0.4 or 0.5 inch, and varying in length from 12 to 18 inches: this kind of glass bears a moderate red heat without softening enough to lose its shape. One end of the tube is drawn out to a point as shown in fig. 160, and closed; the other is simply heated to

Fig. 160.

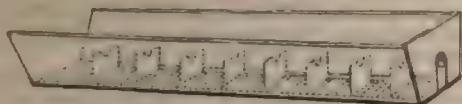
Copper oxide. Mixture. Copper oxide.



soften the sharp edges of the glass. To prevent absorption of moisture by the copper oxide during the filling of the tube, the oxide, when hot, is poured into a long-necked flask closed by a cork; it is then cooled, and afterwards mixed with the organic substance in the combustion tube itself. A small quantity of the cooled oxide is first introduced into the tube, then a portion of the organic substance is added, and then a column of oxide about 3 inches long is poured in the same manner before. This portion of oxide is mixed with the organic substance by drawing it with a clean iron rod, the extremity of which is bent at

To collect the water produced in the experiment, a small light tube of the form represented in fig. 162, or a U-tube, as in fig. 165, filled with fragments of spongy calcium chloride, is attached by a perforated cork, thoroughly dried, to the open extremity of the combustion-tube. The carbon

Fig. 161.



dioxide is absorbed by a solution of caustic potash, of specific gravity 1.27, which is contained in a small glass apparatus on the principle of a Woulfe's bottle, shown in fig. 163. The connection between the latter and the cal-

Fig. 163.

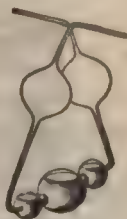


Fig. 162.



cium-chloride tube is completed by a little tube of caoutchouc, secured with silk cord. The whole is shown in fig. 164, as arranged for use.

Fig. 164.



Drawing of the whole arrangement.

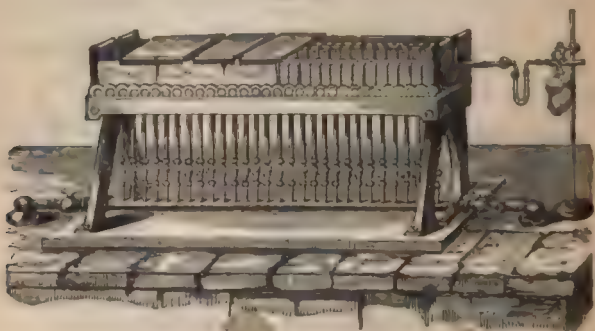
The tightness of the junctions may be ascertained by slightly rarefying the included air by sucking a few bubbles from the interior through the liquid, using the dry lips, or, better, a little bent tube with a perforated cork; if the difference of level in the liquid in the two limbs of the potash apparatus be preserved for several minutes, the joints are perfect. Red-hot charcoal is now placed around the anterior portion of the combustion-tube, containing the pure oxide of copper; and when this is red-hot, the fire is slowly extended towards the farther extremity by shifting the movable screen represented in the drawing. The experiment must be so conducted, that a uniform stream of carbon dioxide shall enter the potash-apparatus by bubbles which may be easily counted; when no nitrogen is present, these bubbles are, towards the termination of the experiment,

almost completely absorbed by the alkaline liquid, the little residue of alone escaping. In the case of an azotized body, on the contrary, bubbles of nitrogen gas pass through the potash-solution during the whole process.

When the tube has been completely heated from end to end, and more gas is disengaged, but, on the other hand, absorption begins to be evident, the coals are removed from the farthest extremity of the combustion-tube, and the point of the latter broken off. A little air is drawn through the whole apparatus, by which the remaining carbon dioxide and watery vapor are secured. The parts are, lastly, detached, and the calcium-chloride tube and potash-apparatus re-weighed.

The mode of heating the combustion-tube with red-hot charcoal is the original process, and is still employed where gas is not available. Since the use of coal gas has been universally adopted in laboratories many contrivances have been suggested, by means of which this convenient fuel may be employed also in organic analysis. An apparatus of this kind* is the one represented in fig. 165, in which the combustion-tube

Fig. 165.

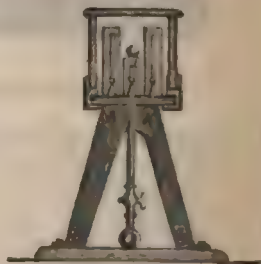


is heated by a series of perforated clay-burners. These clay-burners are fixed on pipes provided with stopcocks, so that the gas may be lighted

Fig. 166.



Fig. 167.



according to the requirements of the case. The stopcocks being appropriately adjusted, the gas burns on the surface of the burners with a steady flame.

* Hofmann, *Journal of Chemical Society*, vol. xi. p. 30.

less blue flame, which renders them in a short time incandescent. The construction of this furnace is readily intelligible by a glance at figures 166 and 167, which exhibit the different parts of the apparatus in section, fig. 166 representing a large furnace with five rows, and fig. 167 a smaller furnace with three rows of clay-burners.

Gas-furnaces of simpler construction, in which the combustion-tube is heated by a row of Bunsen burners, are also much used. Such a furnace as that of von Babo, represented in fig. 169.

The following account of a real experiment will serve to illustrate the calculation of the result obtained in the combustion of crystallized sugar :

| | |
|---|---------------|
| Quantity of sugar employed | 4.750 grains. |
| Potash-apparatus weighed after experiment . . | 781.13 |
| " " before experiment . . | 773.82 |

| | |
|--------------------------|------|
| Carbon dioxide | 7.31 |
|--------------------------|------|

| | |
|---|--------|
| Calcium-chloride tube after experiment . . . | 226.05 |
| " " before experiment . . . | 223.30 |

| | |
|-----------------|------|
| Water | 2.75 |
|-----------------|------|

7.31 gr. carbon dioxide = 1.994 gr. carbon : and 2.75 gr. water = 0.3056 gr. hydrogen ; or in 100 parts of sugar,*

| | |
|---------------------------------|---------------|
| Carbon | 41.98 |
| Hydrogen | 6.43 |
| Oxygen, by difference | 51.59 |
| | <hr/> 100.000 |

When the organic substance cannot be mixed with the copper oxide in the manner described, the process must be modified. If, for example, a volatile liquid is to be examined, it is inclosed in a little glass bulb with a narrow stem, which is weighed before and after the introduction of the liquid, the point being hermetically sealed. A little copper oxide is put into the combustion-tube, then the bulb, with its stem broken at *a*, a scratch having been previously made ; and, lastly, the tube is filled with the cold and dry copper oxide. It is arranged in the furnace, the calcium-chloride tube and potash apparatus adjusted, and then some 6 or 8 inches of oxide having been heated to redness, the liquid in the bulb is, by the approximation of a hot coal, expelled, and slowly converted into vapor, which, in passing over the hot oxide, is completely burned. The experiment is then terminated in the usual manner. Fatty and waxy substances, and volatile solid bodies, as camphor, are placed in little boats of glass or platinum.

Copper oxide which has been used, may be easily restored by moistening with nitric acid, and igniting to redness ; it becomes, in fact, rather improved than otherwise, as, after frequent employment, its density is

Fig. 168.



* The theoretical composition of sugar, $C_{12}H_{22}O_{11}$, reckoned to 100 parts, gives—

| | |
|--------------------|--------------|
| Carbon | 42.11 |
| Hydrogen | 6.43 |
| Oxygen | 51.46 |
| | <hr/> 100.00 |

increased, and its troublesome hygroscopic powers diminished. For substances which are very difficult of combustion, from the large proportion of carbon they contain, and for compounds into which chlorine enters as a constituent, fused and powdered lead chromate may be substituted for the copper oxide, as it freely gives up oxygen to combustible matters, and even evolves, when strongly heated, a little of that gas, which thus insures the perfect combustion of the organic body.

Lead chromate is, however, troublesome to prepare, and always destroys the glass tubes. A more convenient method of insuring the complete combustion of substances which burn with difficulty is to finish the combustion in a stream of oxygen. This may be effected either by placing a small quantity of fused potassium chlorate at the closed end of the combustion-tube, or by connecting the tube with a gas-holder containing oxygen gas. The latter method is to be preferred, as it enables the operator to regulate the stream of gas at his pleasure, whereas the ignition of potassium chlorate is apt to give rise to a rapid evolution of gas, which may force a portion of liquid out of the potash-bulbs and render the analysis worthless.

A form of apparatus for supplying a stream of oxygen is represented in figure 169. The combustion-tube is open at both ends, and the end farthest from the potash-bulbs and calcium-chloride tube is connected with two gas-holders, one filled with air, the other with oxygen gas. The

Fig. 169.



communication is made by means of a T-tube provided with a stopcock, so that either gas-holder may be connected with the combustion-tube and the other shut off at the same time. The air and oxygen, before entering the combustion-tube, are made to pass through two U-tubes, one containing lumps of pumice soaked in sulphuric acid to dry the gas, the other containing lumps of caustic potash to free it from carbonic acid.

The combustion-tube may be heated either with gas or with charcoal (the figure represents a Bunsen's gas apparatus), and the mixture may be disposed in the tube in the way above described—or better, in the case of difficultly combustible bodies—the substance may be placed by itself in a small boat of platinum or porcelain. In this case, the combustion-tube is first filled to two-thirds of its length with copper oxide, which need not be previously ignited, the remaining third, nearest to the gas-holder, being left free to receive the boat. It is then laid in the furnace, and connected in the manner just described with the gas-holder containing atmospheric air; the copper oxide is heated to redness; and a stream of dry air is passed through the tube so as to remove every trace of moisture. The tube is then left to cool; the boat containing the substance is introduced, a plug of recently ignited asbestos having been previously introduced to prevent the copper oxide from coming in contact with it; the calcium-chloride tube and potash-bulbs are attached in the usual manner; and the tube is connected with the gas-holder containing oxygen. The copper

oxide is now once more heated to redness, and as soon as it is thoroughly ignited, heat is very cautiously applied to the part of the tube containing the boat, a slow stream of oxygen being passed through the apparatus, sufficient to prevent any backward passage of the gases, but not to cause any free oxygen to pass through the solution of potash. If the oxide of copper exhibits a red color, indicating reduction, the heating of the substance in the boat must be discontinued till the copper is reoxidized. When at length there is nothing left of the organic substance but black charcoal, the heat may be increased and the stream of oxygen accelerated. In this manner the combustion is soon completed, and when the bubbles of gas appear to pass through the potash without absorption, the process is continued in the same manner for a few minutes longer, and the potash bulb and calcium-chloride tube are then detached, after air has been passed through the apparatus for a little time to displace the oxygen. Lastly, the stream of air is continued for a sufficient time to effect the complete reoxidation of the copper, which is then ready, without further preparation, for another experiment.

After the tube has cooled, the boat is taken out and re-weighed. If any inorganic matter remains in it (as in the case of a salt) the quantity of this is at once ascertained, if the weight of the boat itself is previously known.

As the stream of hot gas is likely to carry vapor of water with it in passing through the potash-bulbs, whence loss of weight would ensue, a second calcium-chloride tube is attached to the potash-bulbs, as shown in the figure, to arrest any water-vapor thus carried over. This tube is weighed, together with the potash-bulbs, before and after the experiment.

The method just described is capable of giving very exact results; it insures the complete combustion of the carbon, and obviates all danger of an excess of hydrogen arising from moisture in the copper oxide. It likewise saves the trouble of igniting this oxide before the experiment and afterwards treating it with nitric acid. But to insure a good result especial care must be taken not to heat the substance in the boat too suddenly; otherwise combustible gases will be given off faster than they can be burnt, and the analysis will be worthless.

Analysis of Azotized Substances.—The presence of nitrogen in an organic compound is easily ascertained by heating a small portion with solid potassium hydrate in a test-tube: the nitrogen, if present, is converted into ammonia, which may be recognized by its odor and alkaline reaction.

In determining the carbon and hydrogen in such bodies, by combustion with copper oxide, as above described, a longer tube than usual must be employed, and 4 or 5 inches of its anterior portion filled with copper-turnings rendered perfectly metallic by ignition in hydrogen. This serves to decompose any nitrogen oxides formed in the process of combustion, which, if suffered to pass off undecomposed, would be absorbed by the potash and vitiate the determination of the carbon.

The nitrogen may be estimated either by converting it into ammonia, by igniting the substance with an alkaline hydrate, as above mentioned, or by evolving it in the free state and measuring its volume.

1. *By conversion into Ammonia:* Will and Varrentrapp's method.—An intimate mixture is made of 1 part caustic soda and 2 or 3 parts quicklime, by slaking lime of good quality with the proper proportion of strong caustic soda, drying the mixture in an iron vessel, and then heating it to redness in an earthen crucible. The ignited mass is rubbed to powder in a warm mortar, and carefully preserved from the air. The lime is useful in many ways: it diminishes the tendency of the alkali to deliquesce, facilitates mixture with the organic substance, and prevents fusion and



ately strong hydrochloric acid, attached by a cork to the con-
tube. Matters being thus adjusted, fire is applied to the tube, com-
with the interior extremity. When it is ignited throughout its
length, and when no gas issues from the apparatus, the point of it
is broken, and a little air drawn through the whole. The acid is
then emptied into a capsule, the bulbs rinsed into the same, first
little alcohol, and then repeatedly with distilled water; an excess
platinic chloride is added; and the whole evaporated to dryness
water-bath. The dry mass, when cold, is treated with a mixture
of alcohol and ether, which dissolves out the superfluous platinum chlor-
leaves untouched the yellow crystalline ammonium platinochlorid
latter is collected upon a small weighed filter, washed with the same
ture of alcohol and ether, dried at 100° , and weighed; 100 parts
spond to 6.272 parts of nitrogen. Or, the salt with its filter may
carefully ignited, the filter burned in a platinum crucible, and the
gen reckoned from the weight of the spongy metal, 100 parts of the
stance being equivalent to 14.18 parts of nitrogen. The former plan
be preferred in most cases.

Bodies very rich in nitrogen, as urea, must be mixed with an
equal quantity of pure sugar, to furnish uncondensable gas, and
diminish the violence of the absorption which otherwise occurs; the
same precaution must be taken, for a different reason, with those
contain little or no hydrogen.

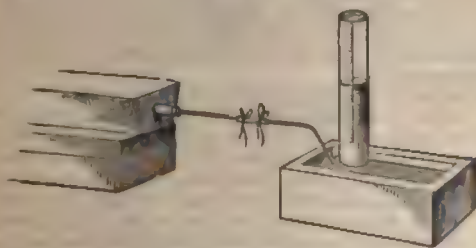
A modification of this process has been suggested by Peligot, and
very convenient if a large number of nitrogen-determinations are

ted in the acid during the combustion. The amount of nitrogen may be calculated. If, for instance, an acid be prepared, containing 20 grain-measures of pure hydrogen sulphate (H_2SO_4) in 1000 grain-measures, then grain-measures of this acid—the quantity introduced into the bulbs correspond with 1.38 grains of ammonia, or 1.14 grains of nitrogen. An alkaline solution is so graduated that 1000 grain-measures will exactly alkalinize the 200 grain-measures of the standard acid. If we now find the acid, partly saturated with the ammonia disengaged during the action of a nitrogenous substance, requires only 700 grain-measures of alkaline solution, it is evident that $\frac{200 \times 300}{1000} = 60$ grain-measures saturated by the ammonia, and the quantity of nitrogen is obtained in proportion— $200 : 1.14 = 60 : x$, wherefore $x = \frac{1.14 \times 60}{200} = 0.342$ grain of nitrogen.

Measurement as free Nitrogen.—When the nitrogen exists in the substance in the form of an oxide, as in nitrobenzene, $\text{C}_6\text{H}_5(\text{NO}_2)$, nitrite, $\text{C}_6\text{H}_5(\text{NO})\text{O}$, etc., the preceding method cannot be employed, as these nitrogen oxides are not completely converted into ammonia acting with alkaline hydrates: it fails also in the case of certain bases. In such cases the nitrogen must be evolved in the free state by heating the organic body with copper oxide; and its volume determined by collecting it over mercury in a graduated jar. There are several ways of effecting this: the one most frequently employed is that of Melsens, as simplified by Melsens.

The tube of Bohemian glass, 28 inches long, is securely sealed at one end; six or seven inches of dry acid sodium carbonate is put to occupy 6 inches. A pure copper oxide is next introduced, and afterwards the mixture of the acid sodium carbonate, the weight of the latter, between 4.5 grains, in a dry state, having been correctly determined. The

Fig. 171.



inner end of the tube, amounting to nearly one-half of its length, is filled up with pure copper oxide and spongy metal, and a round glass tube, perforated by a piece of narrow tube, is securely adapted to its end. This tube is connected by means of a caoutchouc joint with a delivery-tube, *a*, and the combustion-tube is arranged in the furnace. The current of gas is now applied to the further end of the tube, so as to decompose a portion of the acid sodium carbonate, the remainder of the carbonate, as well as the other part of the tube, being protected from the heat by a jacket of sand. The current of carbon dioxide thus produced is intended to displace the air from the apparatus. In order to ascertain that this operation, on which the success of the whole operation depends, is accom-

pinned the delivery-tube is depressed under the level of a mercurial trough, and the gas, which is evolved, collected in a test-tube fitted with concentrated sulphuric acid. If the gas is perfectly absorbed, or, if after the combustion of a considerable quantity, only a minute bubble be left, one may be considered as expelled. The next step is to fill a graduated glass jar two-thirds with mercury and connect with a strong solution of potash, and to insert it over the delivery-tube, as represented in fig. 171.

The flame just is applied to the tube, commencing at the front end and gradually proceeding to the closed extremity, which still contains some leaden chips and sodium carbonate. Thus, when the heat at length reaches it, pushes up carbonic acid, which chases forward the nitrogen lingering in the tube. The carbon dioxide generated during the combustion is wholly absorbed by the potash in the jar, and nothing is left but the nitrogen. When the operation is at an end, the jar, with its contents, is transferred to a vessel of water, and the volume of the nitrogen read off. This is properly corrected for temperature, pressure, and aqueous vapor, and its weight determined by calculation. When the operation has been very successful, and all precautions minutely observed, the result still leaves an error in excess, amounting to 0.3 or 0.5 per cent., due to the residual air of the apparatus, or that condensed in the pores of the copper oxide.

A modification of the process, by which this error is considerably diminished, has been devised by Dr. Maxwell Simpson.*

The method just described is applicable to the estimation of nitrogen in the oxides and oxygen salts of nitrogen, in metallic nitrates and nitres, and, in fact, to the analysis of all nitrogenous bodies whatever.

Analysis of Chlorinated Compounds.—In the case of a volatile liquid containing chlorine, the combustion with copper oxide must be very carefully conducted, and 2 or 3 inches of the anterior portion of the tube kept cool enough to prevent volatilization of the copper chloride into the calcium-chloride tube. Lead chromate is much better for the purpose.

The chlorine is determined by pinning a small weighed bulb of liquid in a combustion-tube, which is afterwards filled with fragments of pure quicklime. The lime is brought to a red heat, and the vapor of the liquid driven over it, when the chlorine displaces oxygen from the lime, and gives rise to calcium chloride. When cold, the contents of the tube are dissolved in dilute nitric acid, the liquid is filtered, and the chlorine precipitated by silver nitrate.

Iodine and Iodine are estimated in a similar manner.

Analysis of Organic Compounds containing Sulphur.—When a body of the nature is burned with copper oxide, a small tube containing lead oxide may be interposed between the calcium-chloride tube and the potash-apparatus, to retain any sulphurous acid that may be formed. It is better, however, to use lead chromate in such cases. The proportion of sulphur is determined by oxidizing a known weight of the substance with strong nitric acid, or by fusion in a silver vessel with ten or twelve times its weight of pure potassium hydrate and half as much nitre. The sulphur is thus converted into sulphuric acid, the quantity of which can be determined by dissolving the fused mass in water, acidulating with nitric acid, and adding a barium salt. *Phosphorus* is, in like manner, oxidized to phosphoric acid, the quantity of which may be determined by precipitation as ammonio-magnesian phosphate.

An easier method of estimating sulphur, phosphorus, chlorine, etc., in organic compounds, consists in heating the substance with nitric acid of specific gravity about 1.2, in a sealed tube. Sulphur is thereby, in nearly

* Quarterly Journal of the Chemical Society, vi. 30.

all cases, completely converted into sulphuric acid, and may be precipitated by chloride of barium; *phosphorus* and *arsenic* are converted into phosphoric and arsenic acids, and may be precipitated as ammonio-magnesium salts; *chlorine* is partly oxidized, partly separated in the free state, but may be completely converted into hydrochloric acid by means of a dilute solution of sulphurous acid or sulphite of sodium, and then precipitated by nitrate of silver; *bromine* and *iodine* are completely separated in the free state, and may be estimated in like manner; lastly, *metals* are converted into oxides or nitrates, and may be estimated by the ordinary methods of mineral analysis.

This method of oxidation by nitric acid in sealed tubes, is likewise applicable to many inorganic compounds, the sulphides of arsenic, for example.

EMPIRICAL AND MOLECULAR FORMULÆ.

A chemical formula is termed *empirical* when it merely gives the simplest possible expression of the composition of the substance to which it refers. A *molecular* formula, on the contrary, expresses the absolute number of atoms of each of its elements supposed to be contained in the molecule, as well as the mere numerical relations existing between them. The empirical formula is at once deduced from the analysis of the substance, reckoned to 100 parts.

The case of sugar, already cited, may be taken as an example. This substance gives by analysis—

| | | | | | | | | |
|----------|---|---|---|---|---|---|---|--------|
| Carbon | . | . | . | . | . | . | . | 41.98 |
| Hydrogen | . | . | . | . | . | . | . | 6.43 |
| Oxygen | . | . | . | . | . | . | . | 51.59 |
| | | | | | | | | 100.00 |

If each of these quantities be divided by the atomic weight of the corresponding element, the quotients will express the relations existing between the numbers of atoms of the three elements: these are afterwards reduced to their simplest expression. This is the only part of the calculation attended with any difficulty. If the numbers were rigidly correct, it would only be necessary to divide each by the greatest divisor common to the whole; but as they are only approximative, something is of necessity left to the judgment of the experimenter.

In the case of sugar, we have—

$$\frac{41.98}{12} = 3.50; \quad \frac{64.3}{1} = 6.43; \quad \frac{51.59}{16} = 3.22,$$

or 350 atoms carbon, 643 atoms of hydrogen, and 342 atoms oxygen. Now it is evident, in the first place, that the hydrogen and oxygen are present nearly in the proportions to form water, or twice as many atoms of the former as of the latter. Again, the atoms of carbon and hydrogen are nearly in the proportion of 12 : 22, so that the formula $C_{12}H_{22}O_{11}$ appears likely to be correct. It is now easy to see how far this is admissible, by reckoning it back to 100 parts, comparing the result with the numbers given by the actual analysis, and observing whether the difference falls fairly, in direction and amount, within the limits of error of what may be termed a good experiment, viz., two or three-tenths per cent. *deficiency* in the carbon, and not more than one-tenth or two-tenths per cent. *excess* in the hydrogen:—

| | |
|--------------------|---------------|
| Carbon | 12 × 12 = 144 |
| Hydrogen | 1 × 22 = 22 |
| Oxygen | 16 × 11 = 176 |

 342

$$342 : 144 = 100 : 42.11$$

$$342 : 22 = 100 : 6.43$$

$$342 : 176 = 100 : 51.46$$

To determine the molecular formula, several considerations must be taken into account, namely, the combining or saturating power of the compound, if it is acid or basic; the number of atoms of any one of its elements (generally hydrogen) which may be replaced by other elements; the law of even numbers, which requires that the sum of the numbers of atoms of all the perissad elements (hydrogen, nitrogen, chlorine, etc.) contained in the compound shall be divisible by 2; and the vapor-density of the compound (if it be volatile without decomposition) which, in normally constituted compounds, is always half the molecular weight (p. 259).

The molecular formula may either coincide with the empirical formula, or it may be a multiple of the latter. Thus, the composition of *acetic acid* is expressed by the formula CH_3O , which exhibits the simplest relations of the three elements; but if we want to express the quantities of these, in atoms, required to make up a molecule of acetic acid, we have to adopt the formula $\text{C}_2\text{H}_4\text{O}_2$: for only one-fourth of the hydrogen in this acid is replaceable by metals to form salts, $\text{C}_2\text{H}_3\text{KO}_2$, for example; and its vapor-density, compared with hydrogen, is nearly 30, which is half the weight of the molecule, $\text{C}_2\text{H}_4\text{O}_2 = 2 \times 12 + 4 \times 1 + 2 \times 16$. Again, the empirical formula of benzene is CH ; but this contains an uneven number of hydrogen atoms, moreover, if it expressed the weight of the molecule of benzene, the vapor-

density of that compound should be $\frac{13+1}{2} = 6.5$, whereas experiment shows that it is six times as great, or equal to 39: hence the molecular formula of benzene is C_6H_6 .

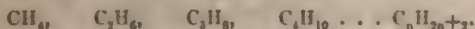
Organic acids and salt-radicles have their molecular weights most frequently determined by an analysis of their lead and silver salts, by burning these latter, with suitable precautions, in a thin porcelain capsule, and noting the weight of the lead oxide or metallic silver left behind. If the lead oxide be mixed with globules of reduced metal, the quantity of the latter must be ascertained by dissolving away the oxide with acetic acid. Or the lead salt may be converted into sulphate, and the silver compound into chloride, and both metals thus estimated. An organic base, on the contrary, has its molecular weight fixed by observation of the quantity of a mineral acid or organic salt-radicle, required to form with it a compound having the characters of neutrality.

The rational and constitutional formulæ of organic compounds will be considered further on.

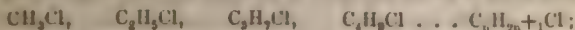
It is scarcely necessary to observe that the methods just described for determining the empirical and molecular formula of an organic compound from the results of its analysis, together with its physical properties and chemical reactions, are equally applicable to inorganic compounds.

CLASSIFICATION OF ORGANIC COMPOUNDS.—ORGANIC SERIES.

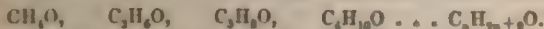
The classification of organic compounds is based upon the quantivalence or atomocity of carbon. This element is a tetrad, being capable of uniting with at most four atoms of hydrogen or other monatomic elements. Methane or marsh gas, CH_4 , is therefore a saturated hydrocarbon, not capable of uniting directly with chlorine, bromine, or other monad elements, but only of exchanging a part or the whole of its hydrogen for an equivalent quantity of another monad element. It may, however, as already explained (p. 237), take up any number of dyad elements or radicles, because such a radicle introduced into any group of atoms whatever, neutralizes one unit of equivalency, and adds another, leaving therefore the combining capacity or equivalence of the group just the same as before. Accordingly, the hydrocarbon, CH_4 , may take up any number of molecules of the bivalent radicle, CH_2 , thereby giving rise to the series of saturated hydrocarbons,



A series of compounds, the terms of which differ from one another by CH_2 , is called a homologous series. There are many such series besides that of the hydrocarbons just mentioned; thus methyl chloride, CH_3Cl , gives, by continued addition of CH_2 , the series of chlorides,

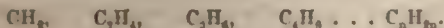


and from methyl alcohol, CH_3O , is derived in like manner the series of homologous alcohols,



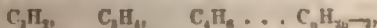
The terms of the same homologous series resemble one another in many respects, exhibiting similar transformations under the action of given reagents, and a regular gradation of properties from the lowest to the highest; thus, of the hydrocarbons, $\text{C}_n\text{H}_{2n+2}$, the lowest terms CH_4 , C_2H_6 , and C_3H_8 , are gaseous at ordinary temperatures, the highest containing 20 or more carbon atoms, are solid, while the intermediate compounds are liquids, becoming more and more viscid and less volatile, as they contain a greater number of carbon atoms, and exhibiting a constant rise of about 20°C . (36°F .) in their boiling points for each addition of CH_2 to the molecule.

The saturated hydrocarbons $\text{C}_n\text{H}_{2n+2}$, may, under various circumstances, be deprived of two atoms, or one molecule, of hydrogen, thereby producing a new homologous series,



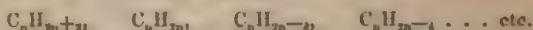
These are unsaturated molecules, having two units of equivalency uncombined, and therefore acting as bivalent radicles, capable of taking up 2 atoms of chlorine, bromine, or other univalent radicles, and 1 atom of oxygen or other bivalent radicle.

The first term of this last series cannot give up 2 atoms of hydrogen without being reduced to the atom of carbon; but the remaining terms may each give up 2 atoms of hydrogen, and thus give rise to the series,



each term of which is a quadrivalent radicle.

And, in like manner, by successive abstraction of H_2 , a number of homologous series may be formed, whose general terms are



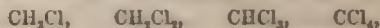
The individual series, as far as C_6 , are given in the following table, together with the names proposed for them by Dr. Hofmann :*

| | | | | | | | |
|-------------|-------------|-------------|----------|----------|----------|----------|--|
| CH_4 | CH_2 | | | | | | |
| Methane | Methene | | | | | | |
| C_2H_6 | C_2H_4 | C_2H_2 | | | | | |
| Ethane | Ethene | Ethine | | | | | |
| C_3H_8 | C_3H_6 | C_3H_4 | C_3H_2 | | | | |
| Propane | Propene | Propine | Propone | | | | |
| C_4H_{10} | C_4H_8 | C_4H_6 | C_4H_4 | C_4H_2 | | | |
| Quartane | Quartene | Quartine | Quartone | Quartune | | | |
| C_5H_{12} | C_5H_{10} | C_5H_8 | C_5H_6 | C_5H_4 | C_5H_2 | | |
| Quintane | Quintene | Quintine | Quintone | Quintune | | | |
| C_6H_{14} | C_6H_{12} | C_6H_{10} | C_6H_8 | C_6H_6 | C_6H_4 | C_6H_2 | |
| Sextane | Sextene | Sextine | Sextone | Sextune | | | |

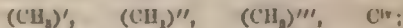
Each vertical column of this table forms a homologous series, in which the terms differ by CH_2 , and each horizontal line an isologous series, in which the successive terms differ by H_2 . The bodies of these last series are designated as the monocarbon, dicarbon group, etc.

The formulæ in the preceding table represent hydrocarbons, all of which are capable of existing in the separate state, and many of which have been actually obtained. They are all derived from saturated molecules, C_nH_{2n+2} , by abstraction of one or more pairs of hydrogen-atoms.

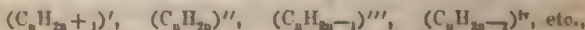
But a saturated hydrocarbon, CH_4 , for example, may give up 1, 2, 3, or any number of hydrogen-atoms in exchange for other elements; thus, marsh gas, CH_4 , subjected to the action of chlorine under various circumstances, yields the substitution-products,



which may be regarded as compounds of chlorine with the radicles,



and in like manner each hydrocarbon of the series, C_nH_{2n+2} , may yield a series of radicles of the forms,



each of which has an equivalent value, or combining power, corresponding with the number of hydrogen-atoms abstracted from the original hydrocarbon. Those of even equivalence contain even numbers of hydrogen-atoms, and are identical in composition with those in the above table; but those of uneven equivalence contain odd numbers of hydrogen-atoms and are incapable of existing in the separate state, except, perhaps, as double molecules (p. 237).

These hydrocarbon radicles of uneven equivalence are designated by names ending in *yl*, those of the univalent radicles being formed from methane, ethane, etc., by changing the termination *ane* into *yl*; those of the trivalent radicles by changing the final *e* in the names of the bivalent

* Proceedings of the Royal Society, xv. 57. Names with Greek prefixes are, however, more generally used: *e. g.*, pentane, hexane, and heptane, rather than quintane, sextane, and septane.

radicles, methene, etc., into *yl*; and similarly for the rest. The names of the whole series will therefore be as follows:—

| | | | | | | | | |
|------------------------|---------------------------|----------------------------|-----------------------------|--------------------------------------|-------------------------------------|--------------------------------------|-------------------------------------|--|
| CH_4 | $(\text{CH}_3)'$ | $(\text{CH}_2)''$ | $(\text{CH})'''$ | | | | | |
| Methane | Methyl | Methene | Methenyl | | | | | |
| C_2H_6 | $(\text{C}_2\text{H}_5)'$ | $(\text{C}_2\text{H}_4)''$ | $(\text{C}_2\text{H}_3)'''$ | $(\text{C}_2\text{H}_2)^{\text{iv}}$ | $(\text{CH})^{\text{v}}$ | | | |
| Ethane | Ethyl | Ethene | Ethenyl | Ethine | Ethinyl | | | |
| C_3H_8 | $(\text{C}_3\text{H}_7)'$ | $(\text{C}_3\text{H}_6)''$ | $(\text{C}_3\text{H}_5)'''$ | $(\text{C}_3\text{H}_4)^{\text{iv}}$ | $(\text{C}_3\text{H}_3)^{\text{v}}$ | $(\text{C}_3\text{H}_2)^{\text{vi}}$ | $(\text{C}_3\text{H})^{\text{vii}}$ | |
| Propane | Propyl | Propene
etc. | Propenyl | Propine
etc. | Propinyl | Propone
etc. | Propenyl | |

From these hydrocarbon-radicles, called alcohol-radicles, because they enter into the composition of alcohols, others of the same degree of equivalence may be derived by partial or total replacement of the hydrogen by other elements, or compound radicles. Thus from propyl, C_3H_7 , may be derived the following univalent radicles:

| | | | | |
|-------------------------------------|---|-------------------------------------|--|------------------------------------|
| $\text{C}_3\text{H}_6\text{Cl}$ | $\text{C}_3\text{H}_5\text{Cl}_2$ | $\text{C}_3\text{H}_5\text{O}$ | $\text{C}_3\text{H}_4\text{Cl}_2\text{O}$ | $\text{C}_3\text{H}_6(\text{CN})'$ |
| Chloropropyl. | Tetrachloro-
propyl. | Oxypropyl. | Trichloro-
oxypropyl. | Cyanopropyl. |
| $\text{C}_3\text{H}_6(\text{NO}_2)$ | $\text{C}_3\text{H}_4(\text{NH}_2)\text{O}$ | $\text{C}_3\text{H}_6(\text{CH}_3)$ | $\text{C}_3\text{H}_5(\text{C}_2\text{H}_5)_2$ | |
| Nitropropyl. | Amidoxypyl. | Methyl-propyl. | Diethyl-propyl. | |

From the radicles above mentioned, all well-defined organic compounds may be supposed to be formed by combination and substitution, each radicle entering into combination just like an elementary body of the same degree of quantivalence.

Organic compounds may thus be arranged in the following classes:—

1. Hydrocarbons containing even numbers of hydrogen atoms.—These are the compounds tabulated on page 478; they are sometimes regarded as hydrides of radicles containing uneven numbers of hydrogen atoms, e.g.,

Methane, $\text{CH}_4 = \text{CH}_3\text{H}$ Methyl hydride.

2. Haloid Ethers.—Compounds of hydrocarbons with halogen elements, e.g.,

| | | |
|------------------------|-----------------------------------|----------------------------------|
| CH_3Cl | $\text{C}_2\text{H}_4\text{Br}_2$ | $\text{C}_3\text{H}_5\text{I}_3$ |
| Methyl chloride. | Ethane bromide. | Propenyl iodide. |

3. Compounds of hydrocarbons with nitryl, NO_2 (the radicle of nitric acid, NO_2OH), e.g.,

| | |
|--------------------------|---------------------------------------|
| CH_3NO_2 | $\text{C}_2\text{H}_4(\text{NO}_2)_2$ |
| Nitro-methane. | Dinitro-methene. |

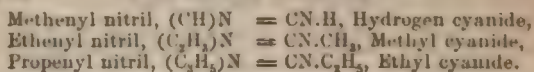
4. Amines and Nitrils.—Compounds of alcohol-radicles with amidegen (NH_2), imidegen (NH)', and nitrogen (N'''): e.g.,

| | | |
|---------------------------------------|---|--------------------------------------|
| $\text{C}_2\text{H}_5\text{NH}_2$ | $(\text{C}_2\text{H}_5)_2\text{NH}$ | $(\text{C}_2\text{H}_5)_3\text{N}$ |
| Ethylamine. | Diethylamine. | Triethylamine. |
| $\text{C}_2\text{H}_4(\text{NH}_2)_2$ | $(\text{C}_2\text{H}_4)_2(\text{NH})_2$ | $(\text{C}_2\text{H}_4)_3\text{N}_3$ |
| Ethene-diamine. | Diethene-diamine. | Triethene-diamine. |

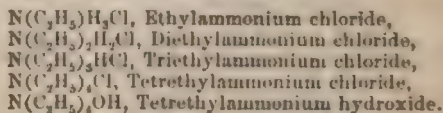
These bodies are mostly of basic character, and capable of forming salts with acids, like ammonia, H_3N , from which they may, in fact, be derived by substitution of alcohol-radicles for part or the whole of the hydrogen. Those in which the hydrogen is wholly thus replaced are called nitrils; and among these special mention must be made of a group consisting of nitrogen combined with a trivalent hydrocarbon-radicle, such as—

| | | |
|-----------------------|--------------------------------|--------------------------------|
| $(\text{CH})\text{N}$ | $(\text{C}_2\text{H})\text{N}$ | $(\text{C}_3\text{H})\text{N}$ |
| Methenyl
nitril. | Ethenyl
nitril. | Propenyl
nitril. |

These nitrils have no basic properties, but are all neutral, except the first, which is a monobasic acid, capable of exchanging its hydrogen for metals, and this character may be regarded as a compound of hydrogen with the equivalent radicle cyanogen— $C\equiv N$; it is accordingly named hydrogen cyanide, or hydrocyanic acid, and the other nitrils homologous with it are the ethers of this acid; thus:

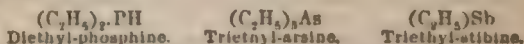


By the combination of amines with the chlorides, hydroxides, etc., of alcohol radicles, compounds are formed containing pentad nitrogen, and having the composition of ammonium salts, in which the hydrogen is more or less replaced by alcohol radicles; thus:

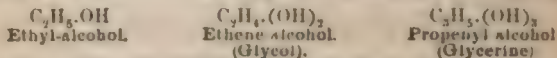


This last compound and its analogues, containing methyl, amyl, etc., are powerful alkalies, obtainable, by evaporation of their aqueous solution, as white deliquescent crystalline masses resembling caustic potash.

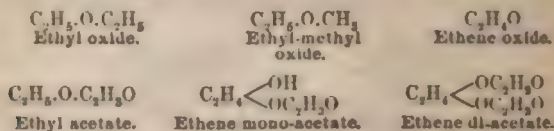
Analogous to the amines are the phosphines, arsines, and stibines,—*e. g.*,



5. Alcohols.—Compounds of hydrocarbons with hydroxyl: *e. g.*,

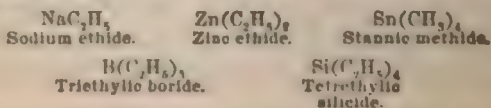


6. The replacement of the hydroxylic hydrogen in an alcohol by hydrocarbon-radicles (alcohol-radicles), or oxygenated hydrocarbon radicles (acid radicles), gives rise respectively to oxygen-ethers and compound ethers, *e. g.*,



7. Sulphur and Selenium Alcohols and Ethers.—Compounds analogous to the oxygen alcohols and ethers—the oxygen being replaced by sulphur or selenium. The sulphur and selenium alcohols are called mercaptans.

8. Compounds of hydrocarbon radicles with various elements, metallic and non-metallic: *e. g.*,



Those containing metals are called *Organo-metallic Compounds*.

1. Aldehydes.—Compounds intermediate between alcohols and acids.

C_2H_5O
Ethyl
alcohol.

C_2H_4O
Acetic
aldehyde.

$C_2H_3O_2$
Acetic
acid.

2. Ketones.—Bodies derived from aldehydes by the replacement of 1 atom of hydrogen by an alcohol-radicle; e. g.,

Acetone, $C_3H_6O = C_2H_5(CH_3)O$.

3. Organic Acids.—Compounds of oxygenated radicles with hydroxyl;

$C_2H_3O_2.HO$
Acetic acid.

$(C_2H_3O_2)_2.(HO)_2$
Succinic acid.

$(C_6H_5O_4)_2.(HO)_2$
Citric acid.

The hydrogen in the radicles of these acids may be more or less replaced by chlorine, bromine, nitril, amidogen, etc.: thus from benzoic acid, $H_5C_6O_2.HO$, are derived:

$C_6H_4ClO_2.HO$
Chlorobenzoic
acid.

$C_6H_4(NO_2)O_2.HO$
Nitrobenzoic acid.

$C_6H_3(NH_2)_2O_2.HO$
Diamidobenzoic
acid.

4. Acid Halides, also called Chlor-anhydrides, Bromanhydrides, etc.—Compounds of oxygenated radicles (acid radicles) with halogen-elements, and derived from the acids by substitution of those elements for the hydroxyl; e. g.,

$C_2H_3O_2.Cl$
Acetyl chloride.

$C_2H_3O_2.Cl_2$
Succinyl chloride.

$C_6H_5O_4.Cl_2$
Citryl chloride.

5. Acid Oxides, sometimes called Anhydrous Acids or Anhydrides;

$(C_2H_3O)_2O$
Acetic oxide.

$C_4H_3O_5O$
Succinic acid.

$C_6H_5O_4 \} O$
 $C_7H_3O_5 \}$
Aceti-benzoic
oxide.

6. Amides.—Compounds analogous to the amines, but containing acid-radicles instead of alcohol-radicles: those which contain bivalent radicles combined with imidogen, NH , are called imides; e. g.,

Acetamide, $C_2H_5O.NH_2$
Diacetamide, $(C_2H_3O)_2.NH$
Succinimide, $C_4H_3O_4.NH$

Succinamide, $C_4H_3O_4(NH_2)_2$
Trisuccinamide, $(C_4H_3O_4)_3.N_3$
Citramide, $(C_6H_5O_4)_3.N$

Each of the classes of carbon compounds above enumerated may be added into homologous and isologous series, though in most cases these are far from being complete.

Further, organic compounds may be divided into two great groups, the Fatty and Aromatic groups, each including hydrocarbons, alcohols, acids, bases, etc., those of the first group being derived from methane, CH_4 , and those of the second from benzene, C_6H_6 . The compounds in these two groups are distinguished from one another by well-marked characters, supposed to depend upon the arrangement of the carbon-atoms in their molecules.

The preceding classes, most of which have their analogues amongst organic compounds, include nearly all artificially prepared organic bodies, and the majority of those produced in the living organism. There still, however, many compounds formed in the bodies of plants and animals, the chemical relations of which are not yet sufficiently well made

and decomposition of compounds, and the relation which allied compounds bear to one another: hence, if a compound can, under varying circumstances, split up into different atomic groups or radicles, or if formed in various ways by the combination of such radicles, rational formulæ must be assigned to it. This point has been noticed in connection with the constitution of metallic salts, and treated especially in the case of the sulphates (p. 285); but organic compounds, which, for the most part, contain larger numbers of atoms, are therefore capable of division into a greater number of groups, and afford much more abundant illustration of the same principle. Take, for example, acetic acid, the molecular formula of which is $C_2H_4O_2$. It may be resolved into the following rational formulæ:—

1. $C_2H_3O_2.H$.—This formula, analogous to that of hydrochloric acid, $Cl.H$, indicates that a molecule of acetic acid can give up one atom of hydrogen in exchange for a univalent metal or alcohol-radicle, for example, sodium acetate, $C_2H_3O_2.Na$, ethyl acetate, $C_2H_3O_2.C_2H_5$, &c.; or two molecules of the acid may give up two hydrogen atoms in exchange for a bivalent metal or alcohol-radicle, forming barium acetate, $(C_2H_3O_2)_2.(C_2H_4)$, etc.; in other words, that acetic acid is a monobasic acid (p. 285).

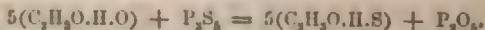
2. $C_2H_3O.HO$.—This formula, analogous to that of water, $H.O$, indicates such reactions as the formation of acetic acid from acetic chloride by the action of water:—



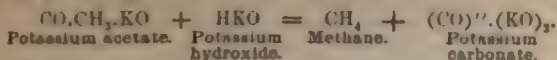
3. $C_2H_3O.H.O$.—This formula, also comparable with that of water, indicates the conversion of acetic acid into acetic chloride, by the action of phosphorus pentachloride:—



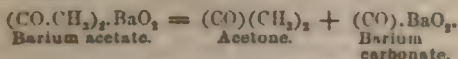
also, the formation of thiactic acid, $C_2H_3O.H.S$, by the action of phosphorus pentasulphide on acetic acid:—



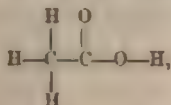
6. The production of methane (marsh-gas) by heating potassium acetate with excess of potassium hydroxide (p. 165).



7. The production of acetone and barium carbonate by the dry distillation of barium acetate:—



Now, on comparing these several rational formulae, it will be seen that they are all included under the constitutional formula,



in which the molecule is resolved into its component atoms, and these atoms are grouped, as far as possible, according to their different equivalents, or combining capacities. These constitutional formulae are the nearest approach to the representation of the true constitution of a compound that our knowledge of its reactions enables us to give; but the student cannot too carefully bear in mind that they are not intended to represent the actual arrangement of the atoms in space, but only, as it were, their relative mode of combination, showing which atoms are connected together directly, and which only indirectly, that is, through the medium of others. Thus, in the formula of acetic acid, it is seen that three of the hydrogen atoms are united directly with the carbon, while the fourth is united to it only through the medium of oxygen; that one of the two oxygen atoms is combined with carbon alone, the other both with carbon and with hydrogen; and that one of the carbon atoms is combined with the other carbon atom and with hydrogen; the second with carbon and with oxygen. Abundant illustration of these principles will be afforded by the special descriptions of organic compounds in the following pages.

Isomerism.—Two compounds are said to be isomeric, when they have the same empirical formula or percentage composition, but exhibit different properties. A few examples of isomerism are met with amongst inorganic compounds; but they are much more numerous amongst organic or carbon compounds.

Isomeric bodies may be divided into two principal groups, namely:—

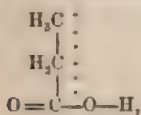
A.—Those which have the same molecular weight; and these are subdivided into:—

1. **Isomeric bodies**, strictly so called, namely, those which exhibit analogous decompositions and transformations when heated, or subjected to the action of the same reagents, and differ only in physical properties. Such is the case with the volatile oils of turpentine, lemons, juniper, etc., all of which have the composition $\text{C}_{10}\text{H}_{16}$, resemble each other closely in their chemical reactions, and are distinguished chiefly by their odor and their action on polarized light.

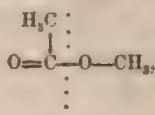
2. **Metameric bodies**, which, with the same percentage composition and molecular weight, exhibit dissimilar transformations under similar circumstances. Thus the molecular formula, $\text{C}_3\text{H}_8\text{O}_3$, represents three

with potash, into potassium formate, $\text{CHO} \cdot \text{OK}$, and ethyl acetate.

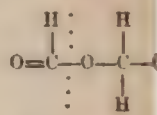
These three compounds may be represented by the following rational formulæ, the dotted lines marking the division into radicals by the rational formulæ above given :—



Propionic acid.



Methyl acetate.



Ethyl formate.

Another kind of metamerism is exhibited by the normal and isomeric alcohols and their derivatives, the structure of which will be explained later.

B.—Compounds which have the same percentage composition, but different molecular weight; such bodies are called polymeric. A striking example of polymerism is exhibited by the hydrocarbons, all of which are multiples of the lowest, namely, methane, CH_4 . An example is afforded by certain natural volatile oils, which are, for instance, with oil of turpentine, $\text{C}_{10}\text{H}_{16}$, and have the formulæ, $\text{C}_{20}\text{H}_{32}$, &c. All polymeric compounds exhibit regular gradations of boiling point, density, and other physical characters, from the lowest to the highest. Some are chemically isomeric, exhibiting analogous transformation reactions under given circumstances, while others are metameric, exhibiting different reactions under given circumstances.

PHYSICAL PROPERTIES OF CARBON-COMPOUNDS.

1. **Density and Specific Volume**—It has been already pointed out (p. 228) that—with a few apparent exceptions depending on dissociation or dissociation at high temperatures—the densities of all gases in the gaseous state are proportional to their molecular weights.

The specific volumes of liquids are comparable only at those temperatures for which their vapor-tensions are equal, as at the boiling points. If the molecular weights are compared with the densities at equal temperatures, no regular relations can be perceived; but when the same comparison is made at the boiling points of the respective liquids, several remarkable laws become apparent. The density of a liquid at its boiling point cannot be ascertained by direct experiment, but when the density at any one point, say at 15.50 C., has been determined, and the rate of expansion is also known, the density at the boiling point may be calculated.

The most important of these relations are the following:—

1. In homologous series a difference of CH_2 in the composition answers to a difference of 22 in the specific volume; thus:

| | | Molecular Weight. | Specific Volume. | Difference. |
|-----------------|-------------------------------------|-------------------|------------------|-------------|
| Formic acid, | CH_2O_2 | 46 | 42 | 22 |
| Acetic acid, | $\text{C}_2\text{H}_4\text{O}_2$ | 60 | 64 | 22 |
| Propionic acid, | $\text{C}_3\text{H}_6\text{O}_2$ | 74 | 86 | 22 |
| Butyric acid, | $\text{C}_4\text{H}_8\text{O}_2$ | 88 | 108 | 22 |
| Valeric acid, | $\text{C}_5\text{H}_{10}\text{O}_2$ | 102 | 130 | 22 |

Hence it follows that the group CH_2 has the specific volume 22.

2. The substitution of 1 atom of carbon for 2 atoms of hydrogen makes no alteration in the specific volume of a liquid compound:

| | | Mol. Wt. | Specific Volume. |
|--------------|-----------------------------------|----------|------------------|
| Octane, | C_8H_{18} | 114 | 187 |
| Cymene, | $\text{C}_{10}\text{H}_{14}$ | 134 | 187 |
| Ethyl ether, | $\text{C}_4\text{H}_{10}\text{O}$ | 74 | 106.8 |
| Phenol, | $\text{C}_6\text{H}_6\text{O}$ | 94 | 106.8 |

Now, since the specific volume of CH_2 is 22, and that of 1 carbon-atom is the same as that of 2 hydrogen-atoms, it follows that the specific volume (or atomic volume) of carbon is 11 and that of hydrogen 5.5.

Calculating in a similar manner the specific volume of oxygen in various carbon-compounds, it is found that this element has two specific or atomic volumes, according as it is united by both its units of affinity to one carbon-atom, as in the group $\text{C}=\text{O}$, in which case its specific volume is 12.2; or to two different atoms, in methyl alcohol, $\text{O} \begin{smallmatrix} \text{CH}_3 \\ \text{H} \end{smallmatrix}$, and methyl

ether, $\text{O} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$, in which case the specific volume is 7.8. In acetic acid,

$\text{CH}_3 \begin{array}{c} | \\ \text{O}=\text{C}-\text{O}-\text{H} \end{array}$, the O-atom which is connected with a carbon-atom alone

has the specific volume 12.2, while that joined to both C and H has the specific volume 7.8. If this compound be represented as acetyl-hydroxide, $\text{CH}_3\text{CO} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \text{O}$, or $\text{C}_2\text{H}_3\text{O} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \text{O}$, that is to say, as water in which 1 atom of hydrogen is replaced by the radicle acetyl, $\text{C}_2\text{H}_3\text{O}$, we may say that the specific volume of the intra-radical oxygen is 12.2, and that of the extra-radical oxygen 7.8.

The specific volume of dyad sulphur varies in a similar manner, being 28.6 or 23 accordingly as the sulphur-atom is united to one atom of another element by both its combining units, or to two separate atoms, as in thiocarbonic acid, $\text{CS} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \text{S}_2$, or $\text{S}=\text{C} \begin{smallmatrix} \text{S}-\text{H} \\ \text{S}-\text{H} \end{smallmatrix}$, where the sulphur-

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atom united with the C alone has the specific volume 28.6, and the two others, each of which is connected both with C and H, have the specific volume 23.

The specific volume of nitrogen in the amines, e. g., $\text{H}_3\text{C}-\text{NH}_2$ (methyl amine), is 2.3; in cyanogen-compounds, 17; and in nitroxyl, NO , 17.4. The specific volumes of the haloid elements are the same in all their compounds, viz., $\text{Cl} = 22.8$; $\text{Br} = 27.8$; $\text{I} = 37.5$.

From these data the specific volumes of compounds may be calculated with very near approach to the values directly obtained by dividing the molecular weights by the specific gravities. A comparison of the observed and calculated values of a few compounds is given in the following table:—

| Substance. | Formula. | Specific Volumes at the Boiling Point. | | |
|-----------------|--|--|-----------|---------------------------------|
| | | Calculated. | | Quotient of Mol. Wt. by Sp. Gr. |
| Water . . . | H_2O | $2 \times 5.5 + 7.8$ | $= 18.8$ | 18.8 |
| Methyl alcohol | $\text{CH}_3.\text{O.H}$ | $11 + 4 \times 5.5 + 7.8$ | $= 40.8$ | 42 |
| Ethyl alcohol . | $\text{C}_2\text{H}_5.\text{O.H}$ | $2 \times 11 + 6 \times 5.5 + 7.8$ | $= 62.8$ | 62.3 |
| Acetic acid . . | $\text{C}_2\text{H}_3\text{O.O.H}$ | $2 \times 11 + 4 \times 5.5 + 7.8 + 12.2$ | $= 64$ | 65.6 |
| Acetone . . . | $\text{CO}(\text{CH}_3)_2$ | $3 \times 11 + 6 \times 5.5 + 12.2$ | $= 78.2$ | 77.6 |
| Butyric acid . | $\text{C}_4\text{H}_7\text{O.OH}$ | $4 \times 11 + 8 \times 5.5 + 7.8 + 12.2$ | $= 108$ | 107 |
| Ethyl acetate . | $\text{C}_2\text{H}_5\text{O.O.C}_2\text{H}_5$ | $4 \times 11 + 8 \times 5.5 + 7.8 + 12.2$ | $= 108$ | 107.6 |
| Mercaptan . . | $\text{C}_2\text{H}_5.\text{S.H}$ | $2 \times 11 + 6 \times 5.5 + 23$ | $= 78$ | 76.1 |
| Aniline . . . | $\text{C}_6\text{H}_5.\text{NH}_2$ | $6 \times 11 + 7 \times 5.5 + 2.3$ | $= 106.8$ | 106.3 |
| Ethyl cyanide | $\text{C}_2\text{H}_5.\text{CN}$ | $3 \times 11 + 5 \times 5.5 + 17$ | $= 77.5$ | 77.2 |
| Ethyl nitrate . | $\text{C}_2\text{H}_5.\text{O.NO}_2$ | $2 \times 11 + 5 \times 5.5 + 17.4 + 3 \times 7.8$ | $= 90.3$ | 90.1 |
| Chloroform . . | CHCl_3 | $11 \times 5 + 3.2 \times 2 \times 8$ | $= 84.9$ | 84.8 |
| Ethyl bromide | $\text{C}_2\text{H}_5.\text{Br}$ | $2 \times 11 + 5 \times 5.5 + 27.8$ | $= 77.3$ | 78.4 |
| Ethyl iodide . | $\text{C}_2\text{H}_5.\text{I}$ | $2 \times 11 + 5 \times 5.5 + 37.5$ | $= 87.0$ | 86.4 |

Melting Point and Boiling Point.—Solid carbon-compounds are for the most part capable of melting without decomposition, and exhibit fixed melting points. Many of those which are liquid at ordinary temperatures boil and volatilize without decomposition under the ordinary atmospheric pressure, and their boiling temperatures are constant under any given pressure. Many others, on the contrary, when heated under the ordinary pressure, decompose before they boil, but some of these are found to boil without decomposition under pressures more or less reduced.

Generally speaking, the boiling point of a compound is higher as its constitution is more complex. This is seen (1) in polymeric compounds: for example, formic aldehyde, CH_2O , is a gas; but acetic acid, $\text{C}_2\text{H}_4\text{O}_2$, is a liquid boiling at 118°C . (244.4°F .); lactic acid, $\text{C}_3\text{H}_4\text{O}_3$, boils at 200°C . (392°F .), but at the same time decomposes to a great extent, and grape sugar, $\text{C}_6\text{H}_{12}\text{O}_6$, is not volatile at all, but undergoes complete decomposition when strongly heated.

In the successive terms of a homologous series, the boiling point increases successively for every addition of CH_2 . In some cases this increase

is very regular: thus in the series of normal alcohols, $C_nH_{2n+1}O$, the successive members, up to the 8-carbon alcohol, differ in boiling point by nearly $19^\circ C.$ ($34.2^\circ F.$), and in the normal fatty acids, $C_nH_{2n}O_2$, the difference from the second to the sixth term is very nearly 22° , but afterwards becomes less; as shown by the following table:—

Alcohols, $C_nH_{2n+1}O$.

| | |
|----------------------|---|
| Ethyl, C_2H_5O | $78.4^\circ C.$ ($173.1^\circ F.$) |
| Propyl, C_3H_7O | $97^\circ C.$ ($206.6^\circ F.$) |
| Butyl, C_4H_9O | $116^\circ C.$ ($240.8^\circ F.$) |
| Pentyl, $C_5H_{11}O$ | $137^\circ C.$ ($278.6^\circ F.$) |
| Hexyl, $C_6H_{13}O$ | $156.6^\circ C.$ ($313.9^\circ F.$) |
| Heptyl, $C_7H_{15}O$ | $177^\circ C.$ ($350.6^\circ F.$) |
| Octyl, $C_8H_{17}O$ | $190-192^\circ C.$ ($374-337.6^\circ F.$) |
| Nonyl, $C_9H_{19}O$ | $200^\circ C.$ ($392^\circ F.$) |

Acids, $C_nH_{2n}O_2$.

| | |
|-----------------------------|---|
| Acetic, $C_2H_4O_2$ | $118^\circ C.$ ($244.4^\circ F.$) |
| Propionic, $C_3H_6O_2$ | $140.6^\circ C.$ ($285^\circ F.$) |
| Butyric, $C_4H_8O_2$ | $163.2^\circ C.$ ($325.9^\circ F.$) |
| Valeric, $C_5H_{10}O_2$ | $184.5^\circ C.$ ($364.1^\circ F.$) |
| Caproic, $C_6H_{12}O_2$ | $204.5^\circ C.$ ($408.2^\circ F.$) |
| Octanthylic, $C_7H_{14}O_2$ | $223-224^\circ C.$ ($434.2-435.2^\circ F.$) |
| Rutic, $C_8H_{16}O_2$ | $232-234^\circ C.$ ($449.6-453.2^\circ F.$) |
| Pelargonic, $C_9H_{18}O_2$ | $253-254^\circ C.$ ($487.4-489.2^\circ F.$) |

In other cases, the differences between the boiling points of the successive members of a series decrease by a regular amount up to a certain term, beyond which they become constant. Thus, in the normal paraffins, C_nH_{2n+2} , the differences decrease regularly by about $4^\circ C.$ ($7.2^\circ F.$) till a constant difference of $19^\circ C.$ ($34.2^\circ F.$) is attained; thus—

| | Boiling point. | Difference. |
|----------------------------|----------------|---------------------|
| Butane, C_4H_{10} | 10° | |
| Pentane, C_5H_{12} | 36° | 37° |
| Hexane, C_6H_{14} | 70° | 32° |
| Heptane, C_7H_{16} | 99° | 29° |
| Octane, C_8H_{18} | 124° | 25° |
| Dodecane, $C_{12}H_{26}$ | 202° | $4 \times 19^\circ$ |
| Hexadecane, $C_{16}H_{34}$ | 271° | $4 \times 19^\circ$ |

In the haloïd ethers and acetic ethers of the alcohol-radicles, C_nH_{2n+1} , the differences of boiling point decrease by about 2° , as shown in the following table:—

| Radicles. | Chlorides,
$C_nH_{2n+1}Cl$ | Bromides,
$C_nH_{2n+1}Br$ | Iodides,
$C_nH_{2n+1}I$ | Acetates,
$C_nH_{2n+1}.C_2H_3O_2$ |
|---------------------|---------------------------------|--------------------------------|------------------------------|--------------------------------------|
| Methyl, CH_3 | | | $40^\circ C.$ $101^\circ F.$ | |
| Ethyl, C_2H_5 | $12.5^\circ C.$ $54.5^\circ F.$ | $39^\circ C.$ $102.2^\circ F.$ | 72° 161.6° | $74^\circ C.$ $165.2^\circ F.$ |
| Propyl, C_3H_7 | 46.4° 115.5° | 71° 159.8° | 101° 215.6° | 102° 215.6° |
| Butyl, C_4H_9 | 77.6° 171.7° | 100.4° 212.7° | 129.6° 265.3° | 125.1° 257.2° |
| Pentyl, C_5H_{11} | 105.6° 222° | 126.7° 263.7° | 153.4° 308.1° | 144.4° 299.1° |
| Hexyl, C_6H_{13} | | | 179.4° 354.9° | 168.7° 334.5° |
| Octyl, C_8H_{17} | 180° 356° | 199° 390.1° | 231° 429.8° | 207° 404.6° |

* Normal carbon-compounds are those in which all the carbon-atoms are linked together in a single chain, e.g., normal butyl alcohol, $CH_3-CH_2-CH_2-CH_2OH$.
 (See HYDROCARBONS, ALCOHOLS, etc.)

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Metameric compounds containing similarly constituted radicals boil for the most part at nearly equal temperatures, *e.g.*,

| Formula, $C_6H_{13}O_2$ | Boiling Point. | | Formula, $C_7H_{15}O_2$ | Boiling Point. | |
|-------------------------|----------------|-----------|-------------------------|----------------|-----------|
| Butyl acetate, | 124.5° C. | 256.1° F. | Pentyl acetate, | 148.4° C. | 299.1° F. |
| Propyl propionate, | 122.4° | 252.3° | Butyl propionate, | 146.0° | 294.8° |
| Ethyl butyrate, | 121.6° | 250.6° | Propyl butyrate, | 143.4° | 290.1° |

Those, on the other hand, which contain differently constituted radicals, boil at different temperatures, the boiling point being lower as the compound has a more complex constitution, or, in other words, as it contains a greater number and variety of radicals: in the butyl alcohols, for example:—

| | | Boiling point. |
|--------------------------|-----------------------|-------------------|
| Normal butyl alcohol, | $C_4H_9.OH$ | 116° C. 240.8° F. |
| Isobutyl alcohol, | $C_4H_9(CH_2)_2.OH$ | 108° 226.4° |
| Secondary butyl alcohol, | $(CH_3)(C_2H_5)CH.OH$ | 96° 203° |
| Tertiary butyl alcohol, | $C(CH_3)_3.OH$ | 92° 197.6° |

Subtraction of hydrogen generally raises the boiling point, *e.g.*,

| | | |
|----------------------|----------------------|----------------------|
| Heptane, C_7H_{16} | Heptene, C_7H_{14} | Heptine, C_7H_{12} |
| 99° C. (210.2° F.) | 100° C. (212° F.) | 107° C. (224.6° F.) |

Hydrocarbons always boil at lower temperatures than their substitution derivatives, the boiling point rising in proportion as a greater amount of hydrogen is displaced.

| | | | | |
|--------------------------|------------------------------|----------------------------------|-----------------------------------|--|
| Ethane, C_2H_6
gas. | Ethyl chloride, C_2H_5Cl | | Ethene chloride, $C_2H_2Cl_2$ | |
| | 12° C. (53.6° F.) | | 82.5° C. (180.5° F.) | |
| | Ethyl alcohol, $C_2H_5.OH$ | | Ethene alcohol, $C_2H_2(OH)_2$ | |
| | 78.4° C. (173.1° F.) | | 197.5° C. (387.5° F.) | |
| Benzene, C_6H_6
82° | Acetic acid, $C_2H_3O.OH$ | | Chloroacetic acid, $C_2H_2ClO.OH$ | |
| | 118° C. (244.4° F.) | | 186° C. (366.8° F.) | |
| | Chlorobenzene,
C_6H_5Cl | Dichlorobenzene,
$C_6H_4Cl_2$ | Trichlorobenzene,
$C_6H_3Cl_3$ | |
| | 135° C. (275° F.) | 172° C. (341.8° F.) | 210° C. (410° F.) | |
| | Amidobenzene, $C_6H_5(NH_2)$ | | Diamidobenzene, $C_6H_4(NH_2)_2$ | |
| | 182° C. (259.6° F.) | | 287° C. (548.6° F.) | |

OPTICAL PROPERTIES.

Refractive Power.—In the chapter on Light (p. 84) it has been explained that the index of refraction of any transparent substance, that is to say, the ratio of the sine of the angle of incidence to the sine of the angle of refraction, is a constant quantity, so long as the density of the substance remains constant.—

$$\frac{\sin i}{\sin r} = n.$$

With variation of density (*d*), and therefore also with variation of temperature, the index of refraction likewise varies; but it has been found,

fact observation made on a large number of substances at different temperatures, that the quantity

$$\frac{n-1}{d},$$

the specific refractive energy, is constant for all temperatures; and this quantity multiplied by the molecular weight of the substance, gives the molecular refractive energy or refraction-equivalent.

The relations between chemical composition and refractive energy have been studied chiefly in bodies of the fatty group (methane-derivatives), the following general laws have been established:—

Isomeric bodies have in many instances equal refraction-equivalents.

In compounds belonging to the same homologous series, the refraction-equivalent increases, in all cases, for a difference of CH_2 , by a nearly equal amount; the mean increment in the fatty alcohols and acids, etc., being 7.60.

The refraction-equivalent of a mixture or compound is equal to the sum of the refraction-equivalents of its components.

His last law gives the means of determining the refraction-equivalents of elements from those of their compounds, the method of calculation being similar to that adopted in the determination of the specific volumes of the elements (p. 485). In the homologous fatty alcohols and acids, the mean values of the refraction-equivalents of carbon, hydrogen, and oxygen are found to be—

| C | H | O |
|------|------|------|
| 5.00 | 1.30 | 3.00 |

From these values the refraction-equivalent of a compound of carbon, hydrogen, and oxygen, may be calculated from the formula

$$R = nr + m'r' + m''r'',$$

where n , m' , m'' , denote the numbers of atoms of the three elements, and r , r' , r'' , their refraction-equivalents.

Thus, for ethyl-alcohol, $\text{C}_2\text{H}_5\text{O}$, the calculated value is

$$2 \times 5 + 6 \times 1.3 + 3 = 20.8.$$

On the other hand, direct observation gives

$$d = 0.7964; \quad n = 1.3606; \quad \text{therefore } \frac{n-1}{d} = 0.4526;$$

and multiplying this number by 46, the molecular weight of alcohol, we obtain for the refraction-equivalent the number 20.8, agreeing exactly with the calculated value.

In like manner for acetic acid, $\text{C}_2\text{H}_4\text{O}_2$, we have

$$2 \times 5 + 4 \times 1.3 + 2 \times 3 = 21.2,$$

for the direct determination—

$$d = 1.053; \quad n = 1.372; \quad \text{mol. wt.} = 60.$$

$$\text{Therefore } \frac{n-1}{d} \times 60 = 0.3533 \times 60 = 21.2.$$

The specific refractive energy of a mixture is the mean of that of its constituents, so that if we know what compounds are present in a mixture, the determination of the specific refractive energy of the mixture (those of

the components being known) affords the means of estimating the quantities of each. For example, a mixture of 81.3 per cent. amyl alcohol, $C_5H_{12}O$, and 18.7 ethyl alcohol, C_2H_6O , was found to have an index of refraction which gave $\frac{n-1}{d} = 0.4940$. Now the mode of calculation above explained

gives for ethyl alcohol $\frac{n-1}{d} = 0.4528$, and for amyl alcohol, 0.5033.

Hence, putting x and y for the relative quantities of ethyl and amyl alcohols in the mixture, we have the two equations—

$$\begin{aligned} x + y &= 100 \\ 0.4528x + 0.5033y &= 49.4 \end{aligned}$$

whence $x = 18.4$; $y = 81.5$, values agreeing very nearly with the quantities actually mixed.

This method of optical analysis affords a convenient method of determining the proportions in which any two substances are mixed, in cases when a separation of the two cannot easily be effected by chemical or physical means, as when they differ but slightly in boiling point, solubility, or other quality which might otherwise be available for separation.

The composition of chemical compounds may, in many cases, be determined in a similar manner.

In certain series of carbon compounds, viz., the hydrocarbons of the aromatic group, including benzene, C_6H_6 , and its homologues—a series of organic bases homologous with pyridine, C_5H_5N , and choline, C_5H_7N —and in certain oxidized essential oils, the refraction-equivalent values are found to be considerably higher than those calculated as above from the values of the elements. The deviations from the normal values exhibit a certain regularity, depending on the composition, which, in the typical hydrocarbons of the several series, may be represented as follows:

| | | Refraction equivalent. | |
|-----------------------------|----------------|------------------------|------|
| Paraffins, | C_nH_{2n+2} | Normal | |
| Olefines, | C_nH_{2n} | " | |
| Terpenes, | $C_{10}H_{16}$ | " | + 3 |
| Benzene and its homologues, | C_nH_{2n-6} | " | + 6 |
| Naphthalene, | $C_{10}H_8$ | " | + 14 |
| Anthracene, | $C_{14}H_{10}$ | " | + 17 |

Similar relations are exhibited by a series of oxidized compounds differing from one another only in their amount of hydrogen:—

| | | | |
|--------------------------|-----------------|--------|------|
| Peppermint camphor, | $C_{10}H_{16}O$ | Normal | |
| Dihydrate of cajuputene, | $C_{10}H_{18}O$ | " | |
| Wormwood oil, | $C_{10}H_{16}O$ | " | + 1 |
| Carvol, | $C_{10}H_{14}O$ | " | + 6 |
| Anethol, | $C_{10}H_{12}O$ | " | + 13 |

Circular Polarization.—The power of turning the plane of polarization of a ray of light to the right or to the left, possessed by many organic compounds, even in the liquid state or in solution, has already been mentioned in the chapter on Light (p. 93), which also contains a description and figure of an instrument used for measuring the amount of power. Substances possessing this power are said to be optically active, or to possess optical rotatory power, dextro-

lævo-; such are amyl alcohol, turpentine oil, camphor, various kinds of sugar and several vegetable acids and alkaloids.

The angle of rotation (α) for any particular ray of the spectrum, the line D, for example—produced by any particular liquid, is proportional to the length of the column of liquid traversed by the ray, and to the quantity of active substance contained in it; and the quantity $[\alpha]$, given by the expression

$$[\alpha] = \frac{\alpha}{d \cdot l},$$

in which α is the observed angle of rotation, d the weight of substance in 1 gram of the solution, l the specific gravity of the solution, and l the length of the column (in decimeters), is called the specific rotatory power. It is constant for each substance at a given temperature.

For example, by dissolving 11.347 grams of grape-sugar in 88.653 grams of water, a solution is obtained, having a specific gravity of 1.048, and producing in a tube 2 decimeters long, a rotation of 13.7° . Hence, the molecular rotatory power of grape-sugar is given by the equation,

$$[\alpha] = \frac{13.7}{0.11347 \times 2 \times 1.048} = 57.6.$$

The power of circular polarization appears to depend on a certain want of symmetry in the molecules of the active substance, and in crystallized bodies it is usually associated with the existence of hemihedral faces. This connection is strikingly exhibited by the isomeric bodies, tartaric and racemic acid, $C_4H_4O_6$. Racemic acid, the crystals of which are holohedral, has no action on polarized light; but, by certain processes to be explained hereafter (see TARTARIC ACID), it may be separated into two isomeric acids, called dextro- and lævo-tartaric acids, the former of which (ordinary tartaric acid) turns the plane of polarization to the right, the latter to the left; and the crystals of these acids are perfectly similar in form, excepting that they possess certain hemihedral faces, occupying opposite positions on the crystal, so that the two crystals are not superposable, but are related to one another like the two hands, or the two sides of the face, or an object and its reflected image. Moreover, the union of these two oppositely active tartaric acids preproduces racemic acid with its original properties, optically inactive, and forming holohedral crystals.

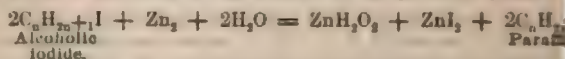
Artificially prepared carbon compounds are, for the most part, active or inactive, according to the character of the compounds from which they are derived. Thus malic acid, prepared by the action of hydriodic acid on tartaric acid, or by that of nitrous acid on asparagin or on optically active aspartic acid, is itself optically active, like the malic acid of fruits; but inactive aspartic acid heated with nitrous acid, yields a malic acid which has no action on polarized light. Recently, however, it has been found that inactive tartaric acid may be converted by a strong heat into dextro-tartaric acid.

the following terms may be called, *heptane, octane, nonane, decane, dodecane*, etc.

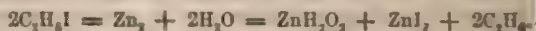
Occurrence and Formation.—Many of the paraffins occur ready in American petroleum and other mineral oils of similar origin. They are formed artificially by the following processes:—

1. By the simultaneous action of zinc and water on the alcohol (p. 479), compounds derived from these same hydrocarbons by the substitution of one atom of iodine for hydrogen.

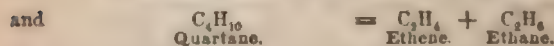
This reaction, which appears to be applicable to the formation of the whole series of paraffins, is represented by the general equation:



As an example, we may take the formation of ethane from ethyl iodide:—



2. All the paraffins may be produced by heating the alcohol with zinc alone. Generally speaking, however, two of these hydrocarbons are obtained together, the first product of the reaction being a compound containing twice as many carbon atoms as the alcoholic iodide and this compound being then partly resolved into the paraffin of half this number of carbon atoms, and the corresponding olefin thus:—



Generally:—



We may suppose that the two molecules of acetic acid are resolved by the current into H_2 and $C_2H_4O_2$, and that the latter then splits up into $2CO_2$ and C_2H_2 . The general reaction is:—



4. Some of the paraffins are obtained from the acids of the series $H_nH_{2n}O_2$ and $C_nH_{2n-2}O_2$, by the action of alkalis, which abstract carbon dioxide from those acids, the hydrocarbon thus eliminated containing one or two atoms of carbon less than the acid from which it is produced. In this manner methane (marsh-gas) is obtained by heating potassium acetate with potassium hydroxide (p. 164).



Also, hexane and octane, by similar treatment of the potassium salts of suberic acid, $C_8H_{15}O_4$, and sebacic acid, $C_{10}H_{19}O_4$:—



Generally speaking, however, a further decomposition takes place, resulting in the formation of hydrocarbons containing a smaller proportion of hydrogen than the paraffins.

5. The paraffins may also be produced from the olefines, C_nH_{2n} , by combining the latter with bromine, and heating the resulting compound, $C_nH_{2n}Br_2$, with a mixture of potassium iodide, water, and metallic copper. The bromine compound is then decomposed, and the hydrocarbon, C_nH_{2n} , is partly reproduced in the free state, partly converted, by addition of hydrogen, into a paraffin.

6. Several of the paraffins are produced by the dry or destructive distillation of butyrates and acetates.

7. They are also found amongst the products of the dry distillation of coal, especially Boghead and Cannel coal, and, as already observed, they constitute the principal portion of many mineral oils, called *petroleum*, *naphtha*, or *rock-oil*, formed by the gradual decay or decomposition of vegetable matter beneath the earth's surface. By far the largest quantities of these oils are obtained from Canada, Pennsylvania, and other parts of North America. Abundant petroleum springs exist, also, on the north-west of the Caspian Sea, near Baku, at Rangoon in Burmah, and in various parts of Italy. The American petroleum consists almost wholly of paraffins. Burmese tar contains, also, small quantities of hydrocarbons belonging to other series, especially homologues of benzene.

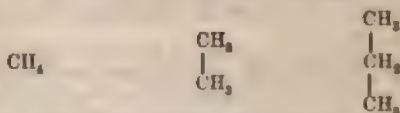
Properties and Reactions of the Paraffins.—Methane, ethane, propane, and butane are gaseous at ordinary temperatures; most of the others are liquids, regularly increasing in specific gravity, viscosity, boiling point, and vapor-density, as their molecular weight becomes greater; those containing 20 carbon-atoms or more are crystalline solids.

The paraffins are saturated hydrocarbons, incapable of uniting directly with monatomic elements or radicals, but they easily yield substitution-derivatives. When subjected to the action of *chlorine* or *bromine*, they give up a part, or in some cases the whole, of their hydrogen in exchange for the halogen element. Thus equal volumes of chlorine and methane, CH_4 , exposed to diffused daylight, yield the compound CH_3Cl , called *chloromethane* or *methyl chloride*; and by further subjecting this product to the action of an excess of chlorine in direct sunshine, it may be succe-

sively converted into the more highly chlorinated compounds CH_3Cl , CHCl_3 , CCl_4 . Ethane, C_2H_6 , also yields, by a series of processes to be presently described, the products $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_4\text{Cl}_2$, $\text{C}_2\text{H}_3\text{Cl}_3$, $\text{C}_2\text{H}_2\text{Cl}_4$, C_2HCl_5 , and C_2Cl_6 ; and similarly for the other compounds of the series. These bodies, which may be regarded as compounds of chlorine and other halogen elements with the radicles $(\text{CH}_3)'$, $(\text{CH}_2)''$, $(\text{CH})'''$, etc., are called haloid ethers. When treated with water or aqueous alkalis, they exchange the haloid element for an equivalent quantity of hydroxyl, (HO) , thereby producing alcohols (p. 480); and, on the other hand, they may be formed from the alcohols by the action of the chlorides, bromides, and iodides of hydrogen or phosphorus.

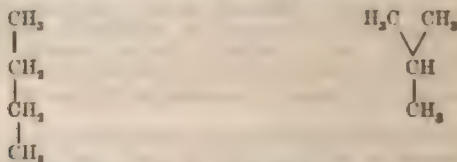
Nitric acid attacks the higher members of the paraffin series, forming nitro-compounds; octane, C_8H_{18} , thus treated, yields the compound, $\text{C}_8\text{H}_{17}(\text{NO}_2)$. The lower paraffins, on the other hand, are not affected by nitric acid; but by indirect means compounds may be formed, having the composition of paraffins in which the hydrogen is more or less replaced by nitril: for example, nitro-methane, $\text{CH}_3(\text{NO}_2)$; tri-nitromethane or nitroform, $\text{CH}(\text{NO}_2)_3$.

The first three hydrocarbons of the series, viz., CH_4 , C_2H_6 , C_3H_8 , exhibit exactly the same physical and chemical properties in whatever way they may be prepared: and indeed the constitutional formulæ of these bodies, viz:



show that they are not susceptible of isomeric modifications, inasmuch as there is but one way in which the carbon-atom in either of them can be grouped; in ethane each carbon-atom is directly combined with three hydrogen-atoms and the other carbon-atom; and whether we regard it as ethyl hydride, $\text{H}-\text{CH}_2\text{CH}_3$, or as dimethyl, $\text{H}_3\text{C}-\text{CH}_3$, this arrangement remains the same. In propane, C_3H_8 , each carbon-atom is directly combined with at most two other carbon-atoms, and there is no other way in which the atoms can be arranged.

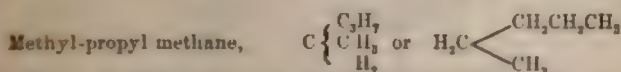
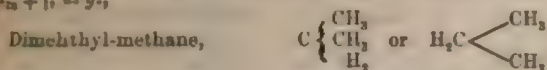
But if we look at the formula of the 4-carbon paraffin, C_4H_{10} , we see that it may be written in either of the following forms:—



In the first of which, neither of the carbon-atoms is directly united with more than two others, whereas, in the second, one of the carbon-atoms is directly combined with three others. The first may be represented, either as propyl-methane, $\text{C} \left\{ \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{H}_3 \end{array} \right\} = \text{C} \left\{ \begin{array}{c} \text{CH}_2\text{C}_2\text{H}_5 \\ \text{H}_3 \end{array} \right\} = \text{C} \left\{ \begin{array}{c} \text{C}_3\text{H}_7 \\ \text{H}_3 \end{array} \right\}$, or as diethyl, $\text{H}_3\text{C}_2\cdot\text{C}_2\text{H}_5$, according to the manner in which we may suppose it to be divided; the second as trimethyl-methane, $\text{C} \left\{ \begin{array}{c} (\text{CH}_3)_3 \\ \text{H} \end{array} \right\}$, or as isopropyl-methane, $\text{C} \left\{ \begin{array}{c} \text{CH}(\text{CH}_3)_2 \\ \text{H}_3 \end{array} \right\}$, the radicle $\text{CH}(\text{CH}_3)_2$ being called isopropyl, to distinguish it from normal propyl, $\text{CH}_2(\text{C}_2\text{H}_5)$.

A comparison of the modes of formation and decomposition of all the paraffins which have been obtained by definite reactions shows that they may be arranged in the four following groups:—*

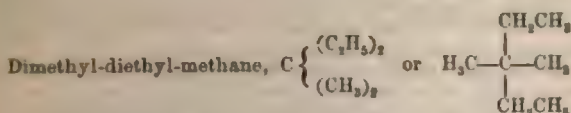
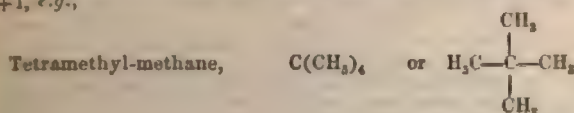
1. **Normal Paraffins**, in which each carbon-atom is directly connected with, at most, *two* other carbon-atoms, or which contain the group or residue CH_2 (methene), associated with two monatomic alcohol-radicles, $\text{C}_n\text{H}_{2n} + 1$, e.g.,



2. **Isoparaffins**, in which one carbon-atom is directly united with *three* other carbon-atoms, or in which the trivalent group or residue, CH (methenyl), is associated with three monatomic radicles, $\text{C}_n\text{H}_{2n} + 1$, e.g.,



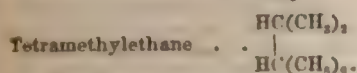
3. **Neoparaffins**, in which one carbon-atom is directly united with *four* other carbon-atoms, or, in other words, with four monatomic radicles, $\text{C}_n\text{H}_{2n} + 1$, e.g.,



The paraffins of these three classes are constructed on the methane type.

4. **Mesoparaffins**, in which two methenyl groups, having their carbon-atoms linked together by one combining unit, are each associated with *two* monatomic radicles, $\text{C}_n\text{H}_{2n} + 1$. These paraffins are, therefore, con-

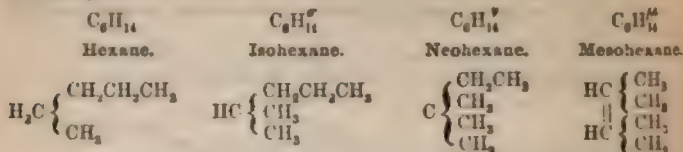
structed on the ethane type, $\begin{array}{c} \text{HCH}_2 \\ | \\ \text{HCH}_2 \end{array}$, e.g.:



The paraffins of the first and second class have for some time been distinguished as *normal* and *iso-paraffins*, and Dr. Odling has lately proposed to distinguish the third class by the prefix *neo* (from *neos*, new, as being the latest discovered), and the fourth by the prefix *meso*, intimating their in-

* Schorlemmer, Proceedings of the Royal Society, xvi 34, 367.

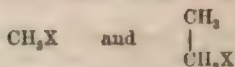
intermediate character, as associated with the iso-paraffins in containing the residue CH , and with the neo-paraffins in containing four alcohol radicals. He also suggests an abbreviated notation, consisting in the use of the Greek letters σ , τ , and μ , as indices of the iso-, neo-, and meso-paraffins respectively, for example:



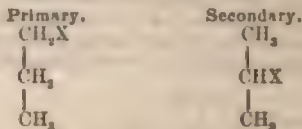
Isomerism in the Substitution-derivatives of the Paraffins.—It has already been stated that the paraffins can exchange one or more of their hydrogen-atoms for various elements and compound radicals, Cl , Br , O , OH , NO_2 , etc., giving rise to alcohols and ethers. Confining our attention for the present to the monatomic derivatives, that is to say, those in which 1 atom of hydrogen is replaced by a univalent radicle X , it is obvious that the first two hydrocarbons of the series

$\text{C}_n\text{H}_{2n+2}$, viz., CH_4 and $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$, can each give rise to only one derivative

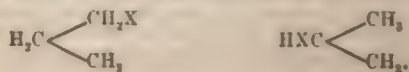
containing any particular monatomic radicle, these derivatives being respectively represented by the formulae—



for supposing, as is most probable, that all the hydrogen-atoms have the same value, and are attached to their respective carbon-atoms in the same way, the result of the substitution must be the same, whichever of these hydrogen-atoms may be thus replaced. But with all the paraffins containing more than two atoms of carbon, the case is different. Thus, in propane, $\text{CH}_3\text{—CH}_2\text{—CH}_3$, the substitution may take place either in one of the exterior groups CH_3 , or in the middle group CH_2 , giving rise to two derivatives of different structure, distinguished by the terms primary and secondary, viz.,



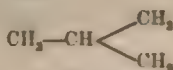
In the primary derivative, the carbon atom joined to the radicle X is connected immediately with only one other carbon atom; in the secondary derivative, it is linked to two other carbon atoms. These are the only possible modifications of a monatomic derivative of the 3-carbon paraffin, C_3H_8 ; they may be more shortly represented by the formula



The 4-carbon paraffin, butane, admits of a greater number of modes of substitution. In the first place, the hydrocarbon itself is susceptible of two modifications, viz:—

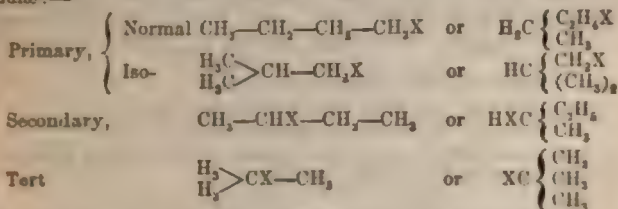


Normal butane.



Isobutane or Trimethyl-methane.

From the first may be formed one primary and one secondary derivative, these terms having the meaning above explained; while the second yields another primary derivative, and likewise a tertiary derivative, in which the carbon atom joined to the radicle X is joined also to three other atoms of carbon. These four derivatives are represented by the following formulæ:—



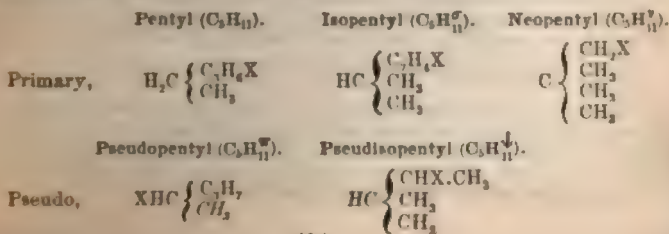
The two primary derivatives are distinguished by containing the radicles normal propyl, $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—}$ and isopropyl $\text{—CH}(\text{CH}_3)_2$ respectively.

Of the four monatomic butane derivatives, the normal primary and the secondary are derived from normal butane, the iso-primary and the tertiary from isobutane.

The higher paraffins yield a larger number of monatomic derivatives according to the nature of the radicles which enter into their constitution; in other words, according as they are either normal, i. e., have all their carbon atoms in a single chain, or contain one or more isopropyl groups,

$\text{HC} \begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$; but these derivatives must all be either primary, secondary, or tertiary; for the carbon atom joined to the radicle X, having one of its combining units thus disposed of, has only three remaining, and cannot therefore be joined to a number of other carbon atoms greater than three. In other words, the replacement of an H-atom by the radicle X must take place either in a methyl residue, CH_3 , a methene residue, CH_2 , or a methenyl residue, CH , producing respectively a primary, secondary, or tertiary derivative.

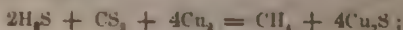
Dr. Odling denotes the secondary and tertiary derivatives by the prefixes *pseudo* and *kato*, distinguishing also the latter by the index α , and the former by the indices π and \downarrow , according as they contain a normal or an iso-radicle, thus—



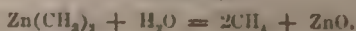
Katapentyl (C_5H_{11}).

We now proceed to describe the more important of the individual paraffins.

Methane, CH_4 , also called *Methyl hydride* and *Murah-gas*, is formed by passing a mixture of hydrogen sulphide and vapor of carbon disulphide over red-hot copper:—



also, by the action of water on zinc-methyl:—



The easiest method of preparing it, however, is to heat a mixture of dry sodium acetate and soda-lime (p. 165):—

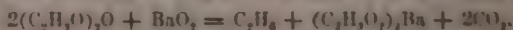


Methane is also produced in the slow decay of vegetable substances, and is found in coal mines as fire-damp, also in marshes and stagnant pools from which it may be evolved as gas by stirring the mud. Lastly, it is formed by the dry distillation of various organic substances, and forms the chief constituent of coal-gas.

Methane is a colorless inodorous gas which burns with a yellow flame, producing water and carbon dioxide. Its density compared with hydrogen as unity is 8, showing that the molecule CH_4 has the normal 2-volume

condensation, $\frac{12 + 4 \times 1}{2} = 8$. When a mixture of equal volumes of methane and chlorine is exposed to sunshine, an explosion takes place, hydrogen chloride being formed, and carbon separated, but in diffused daylight the action goes on slowly, and substitution products are formed, viz., monochloromethane or methyl chloride, CH_3Cl , and with excess of chlorine, also the compounds, CH_2Cl_2 and $CHCl_3$.

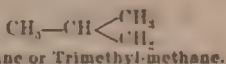
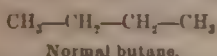
Ethane, C_2H_6 or H_3C-CH_3 .—This compound, which may also be regarded as *dimethyl*, or as *ethyl hydride*, $C_2H_5.H$ (p. 491), is formed by the general reactions already indicated (p. 492), viz., by the action of zinc and water on ethyl iodide; of zinc alone on the same compound, and on methyl iodide; and by the electrolysis of acetic acid, or rather of its potassium salt. It may be prepared in the pure state by decomposing zinc-ethyl with water, or more easily by heating acetic anhydride with barium dioxide—



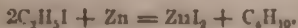
Ethane is a colorless and inodorous gas which has not been liquefied. It is nearly insoluble in water, soluble in about two-thirds of its volume of alcohol. Mixed with an equal volume of chlorine, and exposed to diffused daylight, it forms chloroethane or ethyl chloride, C_2H_5Cl , with excess of chlorine higher substitution products are formed.

Propane, $C_3H_8 = CH_3-CH_2-CH_3$, also called *Methyl-ethyl*, is one of the constituents of petroleum, and may be produced by the action of zinc and hydrochloric acid on propyl iodide or isopropyl iodide. It is a gas which liquefies at $-20^\circ C.$ ($-4^\circ F.$), and dissolves in one-sixth of its volume of alcohol.

Butanes, C_4H_{10} .—Of these compounds, also called *tetranes* or *quaranes*, there are two modifications, viz.:—



1. *Normal butane*, *Diethyl*, or *Methyl-propyl*, occurs in natural petroleum, and in the distillation-products of Cannel and Boghead coal. It may be formed synthetically by heating ethyl iodide to 100° in sealed tubes with zinc:



It is a colorless gas, which condenses below 0° to a liquid boiling at $+1$. Mixed with an equal volume of chlorine, and exposed to light, it yields butyl chloride and other substitution-products.

Isobutane, *Trimethyl-methane*, or *Methyl-isopropyl*, is formed from tertiary butyl iodide, $(CH_3)_3CI$ (p. 497), by the action of zinc and hydrochloric acid. It is a gas which liquefies at $-17^\circ C.$ ($1.4^\circ F.$).

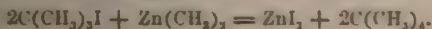
Pentanes, C_5H_{12} .—Of these hydrocarbons there are three modifications, viz.:—

1. Normal Pentane . . . $CH_3-CH_2-CH_2-CH_2-CH_3$
2. Isopentane . . . $CH_3-CH_2-CH \begin{matrix} \swarrow CH_3 \\ \searrow CH_3 \end{matrix}$
3. Neopentane . . . $\begin{matrix} H_3C \\ H_3C \end{matrix} > C < \begin{matrix} CH_3 \\ CH_3 \end{matrix}$

1. *Normal Pentane*, or *Ethyl-propyl*, $C_2H_5-C_3H_7$, occurs in petroleum, and in the light oils of Boghead and Cannel coal, but has not been prepared synthetically. It is a liquid of specific gravity 0.6, and boiling at $37-39^\circ C.$ ($98.6-102.3^\circ F.$). On passing chlorine into its vapor, a primary and a secondary chloride are formed, from which, by a reaction to be hereafter described, the corresponding alcohols may be prepared.

2. *Isopentane* likewise occurs in petroleum, and may be prepared by dehydration of isopentyl alcohol (ordinary amyl alcohol), or by heating the corresponding iodide with water and zinc.

3. *Neopentane*, or *Tetramethyl-methane*, is formed by the action of zinc-methyl on tertiary butyl iodide:—



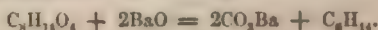
It is a colorless mobile liquid, which boils at $9.5^\circ C.$ ($48.6^\circ F.$), and solidifies at $-20^\circ C.$ ($-4^\circ F.$) to crystals resembling sal ammoniac.

Hexanes, C_6H_{14} .—Of these paraffins, five are possible, and four are known:—

1. Normal Hexane . $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

2. Isohexane, $\left\{ \begin{array}{l} (a) \text{ CH}_3\text{—CH}_2\text{—CH}_2\text{—CH} \begin{array}{l} \swarrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array} \\ (b) \text{ CH}_3\text{—CH} \begin{array}{l} \swarrow \text{CH}_2\text{—CH}_3 \\ \searrow \text{CH}_2\text{—CH}_3 \end{array} \end{array} \right.$
3. Neohexane . . . $\begin{array}{c} \text{H}_3\text{C} \\ \diagup \\ \text{C} \begin{array}{l} \swarrow \text{CH}_2\text{—CH}_3 \\ \searrow \text{CH}_3 \end{array} \\ \diagdown \\ \text{H}_3\text{C} \end{array}$
4. Mesohehexane . $\begin{array}{c} \text{HC}(\text{CH}_3)_2 \\ | \\ \text{HC}(\text{CH}_3)_2 \end{array}$

1. *Normal Hexane*, or *Dipropyl*, occurs in the light oils of Boghead and Cannel coal, and abundantly in Pennsylvanian petroleum. It is formed by the action of sodium on normal propyl iodide, or by that of zinc and hydrochloric acid on secondary hexyl iodide; also by distilling suberic acid with barium oxide:—



It has a density of 0.63 at 17° C. (62.6° F.), and boils at 70–71° C. (158°–159.8° F.).

2. *Isohexane*, *Propyl-dimethyl-methane*, or *Ethyl-isobutyl*, is formed by the action of sodium on a mixture of ethyl iodide and isobutyl iodide, $\text{CH}_3\text{I—CH}(\text{CH}_3)_2$. It has a density of 0.702 at 0°, and boils at 92° C. (143.6° F.).

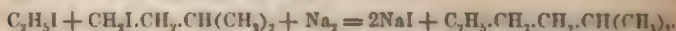
3. *Neohexane*, or *Ethyl-trimethyl-methane*, produced by the action of zinc-methyl on tertiary butyl iodide, boils at 45° C. (113° F.).

4. *Mesohehexane*, or *Di-isopropyl*, formed by the action of sodium on isopropyl iodide, $\text{HC}(\text{CH}_3)_2$, has a density of 0.677 at 0°, and boils at 58° C. (136.4° F.).

Heptanes, C_7H_{16} . Of these hydrocarbons nine are possible and four are known, viz.:

1. *Normal heptane*, $\text{CH}_3\text{—}(\text{CH}_2)_5\text{—CH}_3$, is contained in Pennsylvanian petroleum, and in the light oils of Boghead and Cannel coal, and may be formed by distilling azelaic acid, $\text{C}_9\text{H}_{16}\text{O}_4$, with barium oxide. It has a density of 0.712 at 16° C. (60.8° F.), and boils at 98° C. (208.4° F.).

2. *Ethyl-isopentyl*, or *Ethyl-amyl*, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$, a variety of isoheptane, is formed by the action of sodium on a mixture of ethyl-iodide and isopentyl iodide:



It has a density of 0.683 at 18° C. (64.4° F.), and boils at 90° C. (194° F.).

3. *Triethyl-methane*, $\text{CH}_3\text{—CH}_2\text{—CH} \begin{array}{l} \swarrow \text{CH}_2\text{—CH}_3 \\ \searrow \text{CH}_2\text{—CH}_3 \end{array}$, another variety of isoheptane, is formed by the action of zinc-ethyl on orthoformic ether (see FORMIC ETHERS).



4. *Dimethyl-diethyl-methane*, or *Neoheptane*, $\begin{array}{c} \text{H}_3\text{C} \\ \diagup \\ \text{C} \begin{array}{l} \swarrow \text{CH}_2\text{—CH}_3 \\ \searrow \text{CH}_2\text{—CH}_3 \end{array} \\ \diagdown \\ \text{H}_3\text{C} \end{array}$, is formed by the action of zinc-ethyl on acetone chloride, $(\text{CH}_3)_2\text{CCl}_2$. It has a density of 0.689 at 27° C. (80.6° F.), and boils at 96° C. (204.8° F.).

The higher paraffins have been but little examined. Normal octane, C_8H_{18} , boiling at $124^\circ C.$ ($255.2^\circ F.$), and having a density of 0.703, occurs in petroleum, and is formed—(1) by the action of zinc and hydrochloric acid on normal octyl iodide; (2) by the action of sodium on normal butyl iodide; hence it may be regarded as *dibutyl*, $C_4H_9.C_4H_9$.—*Di-isobutyl*, $(CH_3)_2CH-CH_2-CH_2-CH(CH_3)_2$, obtained by the action of sodium on isobutyl iodide, has a density of 0.705, and boils at $109^\circ C.$ ($228.2^\circ F.$).

Di-isopentyl, $C_{10}H_{22}$, obtained from the iodide of isopentyl (ordinary amyl), has a density of 0.770, and boils at $158^\circ C.$ ($316.4^\circ F.$).

The paraffins of the higher orders are found, together with those already mentioned, in natural petroleum, and in the light oils obtained by the action of heat on various kinds of coal, especially Boghead and Cannel coal.

In most of these products, however, they are mixed with hydrocarbons belonging to other series; and to separate them from these, the crude petroleum or coal-tar oil is mixed with strong sulphuric acid, which removes the olefines and other non-saturated hydrocarbons, and afterwards with fuming nitric acid, or a mixture of strong nitric and sulphuric acids. The hydrocarbons of the benzene series, and all other compounds except the paraffins, are thereby oxidized or converted into nitro-compounds, which are either dissolved by the acid, or are much less volatile than the hydrocarbons. The oils are then washed with water, dried over caustic potash, and rectified over sodium. The distillate thus obtained consists wholly of paraffins, which are separated by fractional distillation.

When thus purified the petroleum and coal-oil paraffins, which boil between 0° and $130^\circ C.$ ($266^\circ F.$) are found to consist of two series; those of the first series, which have the higher boiling points, being normal, while those of the second agree for the most part in boiling point with the corresponding synthetically prepared isoparaffins. The boiling points of the two series are as follows:—

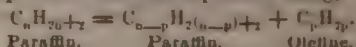
| | | Normal. | | Iso. | |
|----------|-------------|--------------------------------|---------------|---------------------------------|---------|
| Butane, | C_4H_{10} | $0^\circ C.$ ($32^\circ F.$) | | | |
| Pentane, | C_5H_{12} | 36° | 100.4° | $30^\circ C.$ ($86^\circ F.$) | |
| Hexane, | C_6H_{14} | 69° | 156.2° | 61° | 141.8 |
| Heptane, | C_7H_{16} | 98° | 208.4° | 91° | 195.8 |
| Octane, | C_8H_{18} | 124° | 255.2° | 118° | 244.4 |

The boiling points and specific gravities of the higher paraffins of unknown structure, obtained from the same sources, are as follows:—

| | | Boiling point. | | Specific gravity. |
|--------------|----------------|---|-------------------|------------------------|
| Nonane, | C_9H_{20} | $136-138^\circ C.$ ($276.3-280.2^\circ F.$) | | 0.741 at $15^\circ C.$ |
| Decane, | $C_{10}H_{22}$ | $160-162^\circ$ | $320-323.6^\circ$ | 0.757 " 15° |
| Endecane, | $C_{11}H_{24}$ | $180-184^\circ$ | $356-363.2^\circ$ | 0.765 " 16° |
| Dodecane, | $C_{12}H_{26}$ | $196-200^\circ$ | $384.8-392^\circ$ | 0.776 " 20° |
| Tridecane, | $C_{13}H_{28}$ | $216-218^\circ$ | $420.8-421^\circ$ | 0.792 " 20° |
| Tetradecane, | $C_{14}H_{30}$ | $236-240^\circ$ | $456.8-464^\circ$ | |
| Pentadecane, | $C_{15}H_{32}$ | $256-260^\circ$ | $490-500^\circ$ | |

American petroleum likewise yields a quantity of liquid boiling above 300° , and doubtless containing paraffins of still higher order. Some specimens of the crude oil, as it issues from the ground, contain ethane, C_2H_6 , and propane, C_3H_8 , which are given off from it as gas at ordinary temperatures. In boiling for oil also, large quantities of gas escape, exhibiting the characters of methane; hence, it is probable that, in the great geological changes which have given rise to the separation of the petroleum, the whole series of paraffins have been formed, from marsh-gas upwards.

Solid paraffin is a colorless crystalline fatty substance, probably consisting of a mixture of several of the higher members of the series C_nH_{2n+2} . When heated for some time in a sealed tube, it is resolved, with but no evolution of gas, into a mixture of olefines and paraffins of lower molecular weight, which remain liquid at ordinary temperatures. This transformation is easily understood: the hydrocarbon, $C_{70}H_{142}$, for example, might be resolved into $C_2H_2 + C_{68}H_{136}$, or $C_6H_6 + C_{64}H_{128}$, or $C_7H_{14} + C_{63}H_{126}$, etc., the general equation of the decomposition being,



The product actually obtained is a mixture of several paraffins and several olefines.*

Paraffin is found native in the coal-measures, and other bituminous strata, constituting the minerals known as *paraffin wax*, *ozocerite*, *luteolite*, etc. It exists also in the state of solution in many kinds of petroleum, and may be separated by distilling off the more volatile portions, and exposing the remainder to a low temperature. In a similar manner also may solid paraffin be obtained from the tar of wood, coal, and bituminous shale. It was first prepared by Reichenbach from wood-tar. It is tasteless and inodorous, insoluble in water, slightly soluble in alcohol, freely in ether, and miscible in all proportions, when melted, with fixed or volatile oils. It burns with a very bright flame, and those varieties of it which melt at temperatures above $45^\circ C.$ ($113^\circ F.$) are very hard, and well adapted for making candles. Paraffin is largely used also as a substitute for sulphur for dipping matches; and Dr. Stenhouse has patented its application to woollen cloths, to increase their strength and make them waterproof. More extensive, however, are the uses of the liquid compounds of the paraffine series, known in commerce as *paraffin oil*, *photogen*, *solar oil*, *caplane*, etc. These oils are largely used for burning in lamps; and, when mixed with fatty oils, such as rape and cotton-seed oils, form excellent materials for lubricating machinery. For the former purpose they are exceedingly well adapted, as, with a proper supply of air, they give a much brighter light than that obtained from fatty oils containing oxygen, and are much cleaner in use.

It is necessary to observe, however, that natural petroleum and the oils obtained by the dry distillation of coal, etc., at low temperatures, are mixtures of a great number of paraffins differing greatly in volatility, and that to render them safe for burning in lamps of ordinary construction they must be freed by distillation from the more volatile members of the series; otherwise they will take fire too easily, and when they become heated, will give off highly inflammable vapors, which, mixing with the air in the body of the lamp, may easily produce dangerously explosive mixtures, serious accidents have indeed arisen from this cause. It has been found by experience that it is not safe to use paraffin oil which will take fire on the application of a match and burn continuously at a temperature below $35^\circ C.$ ($100.4^\circ F.$).

SECOND SERIES, C_nH_{2n} .—OLEFINS.

The hydrocarbons of this series are polymeric, as well as homologous with one another, inasmuch as their formulae are all exact multiples of that of the lowest, (CH_2) . The lower members of the series are gaseous at

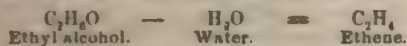
* Thorpe and Young (Berichte der deutschen chemischen gesells., 1874, p. 436).

primary temperatures, the higher members are solid, and the intermediate compounds liquid. The names and formulae of the known members of the olefine series are given in the following table:—

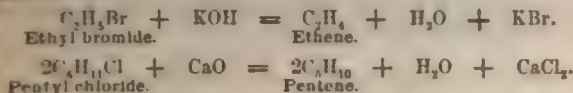
| | | | | | | | | |
|------------------------------|----|------------|---|---|---|---|---|----------------|
| Ethene | or | Ethylene | . | . | . | . | . | C_2H_4 |
| Propene | or | Propylene | . | . | . | . | . | C_3H_6 |
| Tetrene, Butene, or Butylene | | | . | . | . | . | . | C_4H_8 |
| Pentene | or | Amylene | . | . | . | . | . | C_5H_{10} |
| Hexene | or | Hexylene | . | . | . | . | . | C_6H_{12} |
| Heptene | or | Heptylene | . | . | . | . | . | C_7H_{14} |
| Octene | or | Octylene | . | . | . | . | . | C_8H_{16} |
| Nonene | or | Nonylene | . | . | . | . | . | C_9H_{18} |
| Decene | or | Paranylene | . | . | . | . | . | $C_{10}H_{20}$ |
| Hexadecene or Cetene | | | . | . | . | . | . | $C_{16}H_{32}$ |
| Carotene | | | . | . | . | . | . | $C_{27}H_{54}$ |
| Melene | or | Melissene | . | . | . | . | . | $C_{30}H_{60}$ |

Ethene, CH_2 , the lowest term of the series, does not appear to be capable of existing in the separate state.

Formation of the Olefines.—1. By abstraction of the elements of water from the alcohols of the series $C_nH_{2n+2}O$, homologous with common alcohol, under the influence of powerful dehydrating agents, such as oil of vitriol, phosphoric oxide, or zinc chloride; thus:—



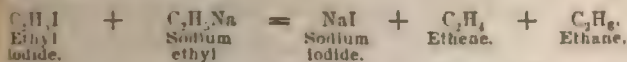
By heating the monatomic haloïd ethers, $C_nH_{2n+1}Br$, etc., with alcoholic solution of potash, or by passing their vapors over lime at a dull heat:—



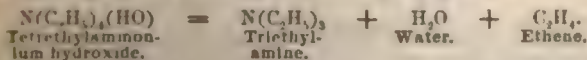
The secondary and tertiary alcohols, and their haloïd ethers are converted into olefines, by this and the preceding reactions, more readily than the primary alcohols. The higher alcohols of the series, $C_nH_{2n+2}O$, undergo this change when merely heated; cetyl alcohol, $C_{16}H_{34}O$, for example, is evolved by distillation into H_2O and cetene, $C_{16}H_{32}$.

By the decomposition of the paraffins, at the moment of their formation, by the action of zinc or sodium on the alcoholic iodides of the monad radical-radicles, C_nH_{2n+1} (see p. 492).

By the action of the same iodides on the sodium-compounds of the monad radical-radicles; for example:



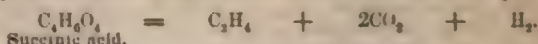
By decomposition of the hydroxides of ammonium bases containing three or atoms of a monad alcohol-radicle (p. 480), these compounds when heated splitting up into a tertiary monamine (p. 487) and an olefine; thus:



Olefines are formed by the decomposition of acetates and butyrates at dull heat, distilling over, together with several other products, from which

they are separated by combining them with bromine, and heating the resulting bromine-compounds, $C_nH_{2n}Br_2$, to 275° with copper, water, potassium iodide. In this manner Berthelot has obtained ethene, propene, butene, and pentene.

7. By electrolysis of the alkali-salts of bibasic acids: e. g.,

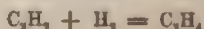


8. By heating the diatomic haloïd ethers, $C_nH_{2n}Cl_2$, etc., with sodium



9. Several of the olefines may be produced by direct synthesis from other hydrocarbons of simpler constitution, or their haloïd derivatives.

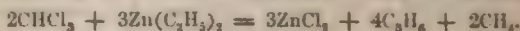
a. Ethene is formed by the action of nascent hydrogen upon ethine acetylene:



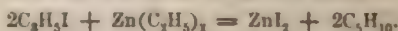
b. Propene, C_3H_6 , is formed by passing a mixture of methane and carbon monoxide (oxymethene) through a red-hot tube:



Also by the action of trichloromethane (chloroform) on zinc ethide:



γ. Pentene, C_5H_{10} , or a compound isomeric or polymeric with it, is formed by the action of zinc ethide on propenyl (allyl) iodide:

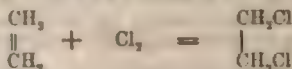


Constitution and Reactions of the Olefines.—These hydrocarbons in the state may be supposed to have one pair of their carbon-atoms linked together by two combining units, thus:

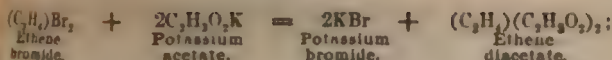


In all the higher members of the series this structure admits of isomeric modifications; three for butene, five for pentene, etc., as will presently be further considered.

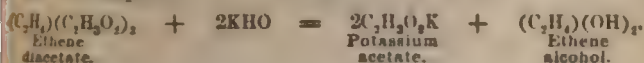
With two carbon-atoms thus doubly linked, the olefines present the appearance of saturated molecules incapable of uniting with monatomic elements or radicles. Under the influence of chlorine, bromine, and iodine, however, they undergo a change of structure, the double linking of two carbon-atoms being partly broken up, so that these atoms remain united by one combining unit only, and the hydrocarbon becomes a divalent radicle, capable of taking up 2 atoms of chlorine, bromine, etc., to



The resulting diatomic ethers, treated with silver acetate or potassium acetate, exchange their bromine for an equivalent quantity of the haloïd residue of the acetate, $C_2H_3O_2$ (p. 481), giving rise to diatomic acetic ethers thus:

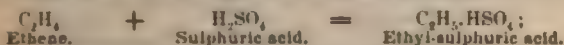


and these ethers, distilled with a caustic alkali, yield diatomic alcohols or polyols, for example:



The bromides, $\text{C}_n\text{H}_{2n}\text{Br}_2$, heated to 275°C . (527°F .) with a mixture of potassium iodide, copper, and water, give up their bromine and reproduce the original olefine, together with other hydrocarbons (p. 493).

Some olefines, when briskly shaken up with strong sulphuric acid, give with it, forming acid ethers of sulphuric acid, which contain the monatomic alcohol-radicles analogous to the olefines; thus:

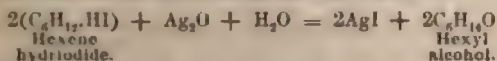


These acid ethers distilled with water reproduce sulphuric acid and monatomic alcohol analogous to the olefine:



In fuming sulphuric acid (which contains sulphuric oxide in solution) the olefines yield sulpho-acids which are isomeric with the preceding, and are not decomposed by water with formation of an alcohol.

Olefines unite with *hydrochloric, hydrobromic, and hydriodic acids*; and the resulting compounds, treated with silver oxide in presence of water, give rise to two different reactions which go on simultaneously, one part of the compound exchanging its halogen element for hydroxyl, and thereby forming an alcohol, while another portion gives up hydrochloric, hydrobromic, or hydriodic acid, reproducing the original olefine:—

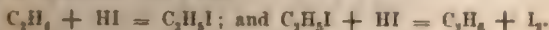


Olefines also unite with *hypochlorous acid*, forming compounds called *oleic chlorhydrins*; e.g.:—



nascent hydrogen (evolved by zinc and hydrochloric acid) they are reduced into paraffins; e. g., $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$.

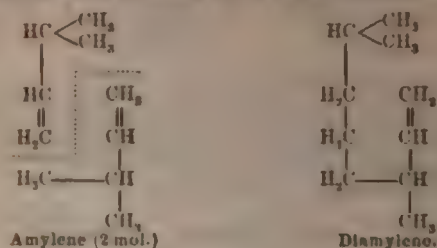
Olefines also yield paraffins when heated with concentrated *hydriodic acid*, the monosoparaffin formed in the first instance being reduced by a second dose of hydriodic acid; e. g.:—



Condensation of the Olefines.—These bodies, under the influence of sulphuric acid, zinc chloride, boron fluoride, and other reagents, even at very low temperatures, become polymerized by the linking together of two or more molecules. In this manner, isopentene or amylene, C_5H_{10} , may be condensed into $\text{C}_{10}\text{H}_{20}$, $\text{C}_{15}\text{H}_{30}$, etc. Propene and butene may also be poly-

merized, but ethene is not polymerized either by sulphuric acid or by boron fluoride. The polymeric hydrocarbons thus formed are dyad radicals, capable of uniting directly with chlorine, etc.

The following diagram exhibits the conversion of isopentene or amylene into di-amylene, showing that the latter also has two of its carbon atoms doubly linked, and may therefore act as a dyad radical:—

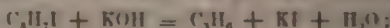


Ethene or Ethylene, C_2H_4 , also called *Olefiant gas*, is produced in the dry distillation of many organic bodies, and is found, to the amount of about 6 per cent., in coal gas. It is most easily prepared by heating strong alcohol with three or four times its weight of strong sulphuric acid (p. 165). It is a colorless inflammable gas, which burns with a bright white flame. When exposed to a strong pressure at a temperature of -110°C . (-166°F .), it condenses to a liquid which does not solidify. Its specific gravity, referred to hydrogen as unity, is 14, showing that the molecule C_2H_4 has the normal 2-volume condensation:—

$$\frac{2 \times 12 + 4 \times 1}{2} = 14.$$

Ethene unites readily with chlorine, bromine, and iodine, forming oily liquids. Fuming hydriodic acid absorbs it, with formation of ethyl iodide $\text{C}_2\text{H}_5\text{I}$. It dissolves also in strong sulphuric acid, after prolonged action at ordinary temperatures, easily and completely at $160-170^\circ \text{C}$. ($320-347^\circ \text{F}$.). The product is ethylsulphuric acid, $\text{C}_2\text{H}_5\text{SO}_3\text{H}$, which, when boiled with water, yields ethyl alcohol. Ethene is oxidized by chromic acid to aldehyde, $\text{C}_2\text{H}_4\text{O}$, and by potassium permanganate to oxalic and formic acid.

Propene, $\text{C}_3\text{H}_6 = \text{CH}_2 - \text{CH} = \text{CH}_2$, is formed (1) By heating propyl iodide or isopropyl iodide with alcoholic potash solution:—



(2) By the action of nascent hydrogen (from zinc and hydrochloric acid) or of hydriodic acid, on allyl iodide:—



(3) Together with other products, by passing the vapor of ordinary and alcohol or butyl alcohol through a red-hot tube. It also occurs in coal gas.

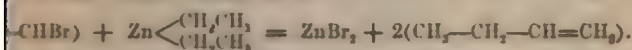
Propene is a colorless gas, condensable to a liquid by strong pressure. It dissolves readily in strong hydriodic acid, forming secondary propyl iodide:



ene, or Butylene, C_4H_8 . Of this hydrocarbon there are three isomers, represented by the following formulae:—

- | | |
|------------------|--|
| 1. Butene, | $CH_3-CH_2-CH=CH_2$; |
| 2. Pseudobutene, | $CH_3-CH=CH-CH_3$; |
| 3. Isobutene, | $\begin{array}{c} H_3C \\ H_2C \end{array} > C=CH_2$. |

Normal butene is produced by abstraction of HI (action of alcoholic from normal primary butyl iodide, $CH_3-CH_2-CH_2-CH_2I$, and by action of zinc-ethide on bromethene:



is gaseous at ordinary temperatures, and condenses at $-10^\circ C.$ ($14^\circ F.$) and which boils at $-5^\circ C.$ ($23^\circ F.$). It unites with hydriodic forming secondary butyl iodide, $CH_3-CH_2-CHI-CH_3$.

Pseudobutene is formed by heating secondary or pseudobutyl or the corresponding alcohol, with alcoholic potash, or with silver. It boils at $+3^\circ C.$ ($37.4^\circ F.$), and solidifies at low temperatures. It unites with HI, reproducing secondary butyl iodide.

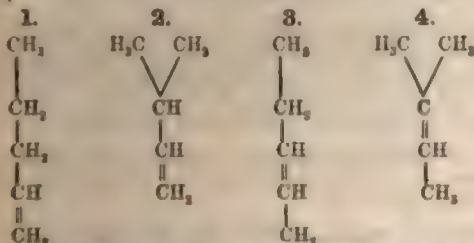
Isobutene is produced by the action of alcoholic potash on isobutyl iodide, $\begin{array}{c} H_3C \\ H_2C \end{array} > CH-CH_2I$, or on tertiary butyl iodide, $\begin{array}{c} H_3C \\ H_3C \end{array} > C-CH_3$, or by action of sulphuric acid on the corresponding alcohols. It is also formed by the vapor of isopentyl alcohol through a red-hot tube, and by hydrolysis of isovaleric (ordinary valeric) acid.

Isobutene is gaseous at ordinary temperatures, but condenses at very low temperatures to a liquid, which boils at $-6^\circ C.$ Strong hydriodic acid acts on it, with formation of tertiary butyl iodide. With sulphuric acid it unites, together with polymeric butenes, tertiary butylsulphuric acid, $\begin{array}{c} CH_3 \\ SO_3H \end{array}$, which, when boiled with water, yields tertiary butyl alcohol.

The bromides of the three isomeric butenes, C_4H_7Br , boil at the following temperatures:—

| Normal. | Iso. | Pseudo. |
|------------------------|----------------------------------|----------------------------------|
| $B. (330.8^\circ F.).$ | $159^\circ C. (318.2^\circ F.).$ | $149^\circ C. (300.2^\circ F.).$ |

Pentenes, C_5H_{10} . Of the four possible modifications of these hydrocarbons, viz.,



Normal Pentene, or Ethyl-allyl, C_5H_8 . It is formed by the action of sodium on a mixture of the iodides of ethyl and allyl, or of zinc-ethyl iodide. It boils at $37^\circ C.$ ($98.6^\circ F.$); unites with hydri-

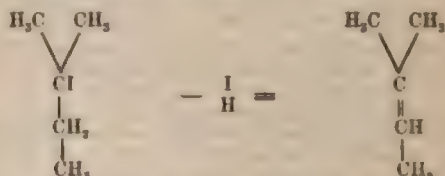
odic acid to form the secondary iodide, $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CHI—CH}_3$, or $\text{IHC} \begin{smallmatrix} \text{CH}_3 \\ \diagup \\ \text{C}_3\text{H}_7 \end{smallmatrix}$. Its bromide, $\text{C}_5\text{H}_{10}\text{Br}_2$, boils at 175°C . (347°F .).

2. *Isopentene*, or *Amylene*, is obtained, together with isopentane, by distilling ordinary amyl alcohol, $\text{H}_3\text{C} \begin{smallmatrix} \text{H}_2\text{C} \\ \diagup \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \text{—CH—CH}_2\text{—CH}_2\text{OH}$, with sulphuric acid or zinc chloride. It is a colorless mobile liquid having a fragrant odor, a density of 0.663 at 0° , and boiling at 35°C . (95°F .). Its bromide boils at $170\text{--}180^\circ\text{C}$. ($338\text{--}356^\circ\text{F}$.), with partial decomposition. Isopentene unites with hydriodic acid, forming another secondary pentyl iodide, $(\text{CH}_3)_2\text{CH—CHI—CH}_2\text{CH}_3$.

Isopentene shaken up with sulphuric acid (previously diluted with half its bulk of water, and cooled) is converted into several polymerides, viz., diamylenes, $(\text{C}_5\text{H}_{10})_2$, boiling at 156°C . (312.8°F .); triamylenes, $\text{C}_{15}\text{H}_{30}$, at $240\text{--}250^\circ\text{C}$. ($460\text{--}482^\circ\text{F}$.); tetramylenes, $\text{C}_{20}\text{H}_{40}$, at 360°C . (644°F .). They are oily liquids, uniting directly with bromine.

3. The third modification is not known with certainty, but is perhaps identical with a pentene, boiling at 25°C . (77°F .), obtained by the action of concentrated alcoholic potash on isopentyl iodide.*

4. The fourth modification is obtained by the action of very strong alcoholic potash on tertiary pentyl iodide:



It boils at 35°C . (95°F .), unites with bromine, and with fuming hydriodic acid at 100° , reproducing the tertiary iodide.†

The higher olefines have been but little studied. They are obtained from the corresponding alcohols and iodides by the methods above described.

Hexene, or **Hexylene**, C_6H_{12} . Two hydrocarbons of this composition have been obtained, one from secondary, the other from tertiary hexyl alcohol. The former has a specific gravity of 0.699 at 10° , and boils at $65\text{--}66^\circ\text{C}$. ($149\text{--}150.8^\circ\text{F}$.); the latter, which occurs in the light oils from Boghead and Cannel tar, boils at 70°C . (158°F .).

Heptene, or **Heptylene**, C_7H_{14} , also called *ananthylene*, is formed from secondary heptyl chloride; also, by treating heptyl aldehyde (ananthol), $\text{C}_7\text{H}_{14}\text{O}$, with phosphorus pentachloride, and decomposing the resulting chloride, $\text{C}_7\text{H}_{14}\text{Cl}_2$, with sodium. It boils at 100° . The same hydrocarbon occurs in the light oils from Boghead and Cannel tar.

Octene, or **Octylene**, C_8H_{16} , occurs in the same oils, and is easily prepared by distilling secondary octyl alcohol with zinc chloride. It boils at 125°C . (257°F .).

Cetene, $\text{C}_{16}\text{H}_{32}$, **Cerotene**, $\text{C}_{27}\text{H}_{54}$, and **Melene**, $\text{C}_{30}\text{H}_{60}$, are formed by destructive distillation of the corresponding alcohols, or sub-

* Flavitzky, Liebig's Annalen, clix. 265

† Ermolaiew, Zeitschrift für Chemie, 1871, 273.

stances containing them; cetene from spermaceti, cerotene from Chinese wax, melene from beeswax.

Cetene is an oily liquid, boiling at 275°C . (527°F .); cerotene, a crystalline solid; melene crystallizes from hot alcohol in scales, which melt at 32°C . (143.6°F .).

THIRD SERIES.— $\text{C}_n\text{H}_{2n-2}$.

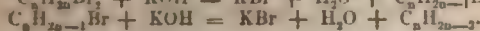
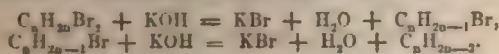
Ethine or Acetylene Series.

These hydrocarbons may be arranged in two collateral series differing from one another in structure and in properties. The following are known:

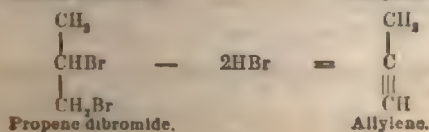
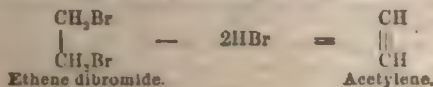
| α Series. | | | Boiling Point. | |
|------------------|------------------------|------------------------------|--|-----|
| Ethine | or Acetylene, | C_2H_2 | ... | ... |
| Propene | " Allylene, | C_3H_4 | ... | ... |
| Pentene | " α Valerylene, | C_5H_8 | 50°C . (122°F .) | |
| Hexene | " Hexoylene, | C_6H_{10} | 80°C . (176°F .) | |
| Heptene | " | C_7H_{12} | 107°C . (224.6°F .) | |
| Octene | " | C_8H_{14} | 133°C . (271.4°F .) | |
| Decene | " Decenylene, | $\text{C}_{10}\text{H}_{18}$ | 165°C . (329°F .) | |
| Pentadecene | " Benylene, | $\text{C}_{15}\text{H}_{26}$ | 225°C . (437°F .) | |
| Hexadecene | " Cetenylene, | $\text{C}_{16}\text{H}_{26}$ | 260°C . (536°F .) | |

| β Series. | | Boiling Point. | |
|---------------------|------------------------------|---|--|
| β Allylene, | C_3H_4 | ... | |
| Crotonylene, | C_4H_6 | 18°C . (64.4°F .) | |
| β Valerylene, | C_5H_8 | 45°C . (113°F .) | |
| Diallyl, | C_6H_{10} | 59°C . (138.2°F .) | |
| Rutylene, | $\text{C}_{10}\text{H}_{18}$ | 150°C . (302°F .) | |

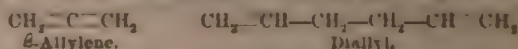
A general method of preparing the hydrocarbons of the α series, consists in heating the dibromides or di-iodides of the olefines with alcoholic potash, the reaction taking place by two stages, a monobrominated olefine being first formed, and then deprived, by the further action of the potash, of the elements of hydrobromic acid; thus—



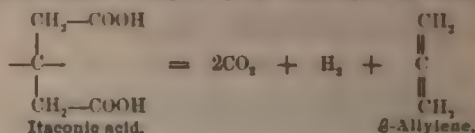
The reaction amounts to the abstraction of 2HBr from the olefine dibromide, and shows that the hydrocarbons of this series have two of their carbon atoms united by three combining units; thus—



Acetylene does not admit of any other modification, at least in the free state; but in allylene, and the higher members of the series, another mode of grouping is possible, as shown by the following formulae:—

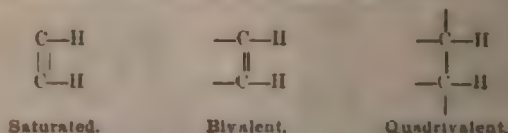


The hydrocarbons of this latter (β) subseries are formed by various reactions, β -allylene, for example, by the electrolysis of itaconic acid:—

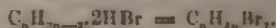


The hydrocarbons of the two subseries likewise differ in certain of their properties. Those of the α series, when treated with an ammoniacal solution of argentic or cuprous chloride, yield metallic derivatives, in the form of crystalline precipitates, which, when heated with hydrochloric acid, reproduce the original hydrocarbons. This reaction affords a convenient method of separating acetylene and allylene from other gases. The hydrocarbons of the β subseries do not yield these metallic derivatives.

When the hydrocarbons of the α subseries are subjected to the action of chlorine, bromine, and other powerful reagents, the connection between the trebly-linked carbon atoms becomes loosened—as in the case of the olefines—so that the molecule which was previously saturated becomes bivalent or quadrivalent: thus, in the case of acetylene,



When agitated with hydrobromic or hydriodic acid, they take up one or two molecules of these acids. The dihydrobromides and dihydriodides thus produced have the same composition as the dibromides of the olefines; thus



The two classes of bodies are, however, isomeric, not identical.

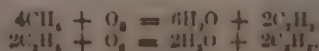
Acetylene, or Ethine, C_2H_2 .—This hydrocarbon is one of the constituents of coal gas.—It is produced—1. By synthesis from its elements. When an electric arc from a powerful voltaic battery passes between carbon poles in an atmosphere of hydrogen, the carbon and hydrogen unite in the proportion to form ethine.

2. By the action of heat upon ethene, or the vapor of alcohol, ether, or wood-spirit, or by passing induction-sparks through marsh-gas.

3. By passing the vapor of chloroform over ignited copper:



4. By the incomplete combustion of bodies containing carbon and hydrogen; for example:

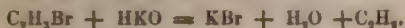


produced in considerable quantity in the imperfect combustion which takes place in a Bunsen's gas-burner, when the flame strikes down and burns at the small orifice at the bottom of the tube; it may be collected and purified by aspirating the gas through an ammoniacal copper or solution.

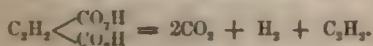
By passing a mixture of marsh-gas and carbon monoxide through a tube:



By the action of alcoholic potash on monobromethene:



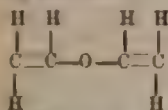
By the electrolysis of fumaric or maleic acid:



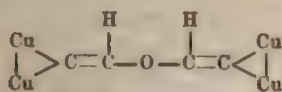
Crude acetylene obtained by either of these processes is purified in manner above mentioned.

Acetylene is a colorless gas of specific gravity 0.92, having a peculiar pleasant odor, moderately soluble in water, not condensed by cold alone. It burns with a very bright and smoky flame, one volume of gas consuming $2\frac{1}{2}$ volumes of oxygen, and producing 2 volumes of carbon dioxide. When mixed with chlorine, it detonates almost instantly, in diffused daylight, with separation of carbon.

Acetylene passed into an ammoniacal solution of cuprous chloride forms a precipitate consisting of cuproso-vinyl oxide, $\text{C}_2(\text{Cu}_2)_2\text{H}_2\text{O}$, or $(\text{C}_2\text{H})_2\text{O}$, that is to say, vinyl-oxide, $(\text{C}_2\text{H}_3)_2\text{O}$, having four of its valence-atoms replaced by four atoms of (apparently) univalent copper (361). The constitution of this compound may be understood from the following formulae:

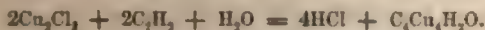


Vinyl oxide.



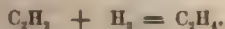
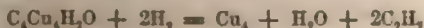
Cuproso-vinyl oxide.

Reaction from cuprous chloride and acetylene is represented by the equation:



Heating it with hydrochloric acid, the opposite reaction takes place, the chloride and water being reproduced, and pure acetylene evolved.

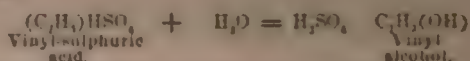
When this copper compound is heated with zinc and dilute ammonia, nascent hydrogen thereby evolved unites with the elements of ethine, forming ethene:



Acetylene, briskly agitated with strong sulphuric acid, is absorbed, producing vinyl-sulphuric acid, $\text{C}_2\text{H}_4\text{SO}_4$:



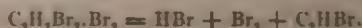
and this acid, distilled with water, is resolved into sulphuric acid and vinyl alcohol:



Acetylene unites with bromine, forming a dibromide, $\text{C}_2\text{H}_2\text{Br}_2$.

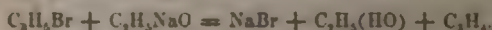
When a series of strong induction sparks is passed through a mixture of acetylene and nitrogen, the two gases unite and form hydrocyanic acid: $\text{C}_2\text{H}_2 + \text{N}_2 = 2\text{CNH}$.

Bromacetylene, C_2HBr , is produced by the action of alcoholic potash on dibromomethene dibromide:



It is a spontaneously inflammable gas, which liquefies under a pressure of three atmospheres, is soluble in water, and very soluble in dibromomethane. It unites with bromine, forming the compound $\text{C}_2\text{HBr}\cdot\text{Br}_2$, and when passed into an ammoniacal solution of cuprous chloride, yields a precipitate of cuproso-vinyl oxide.

Allylene or Propene, C_3H_4 .—This compound is produced by the action of sodium ethylate on bromopropene:



Its formation being a particular case of the general reaction given on page 509. It is a colorless gas, having an unpleasant odor, burning with a smoky flame, and forming, with mercurous salts, a gray precipitate; with silver salts, a white precipitate; and with cuprous chloride, a yellow precipitate, analogous in composition to that formed by ethine. With benzene it forms the compounds $\text{C}_3\text{H}_4\text{Br}_2$ and $\text{C}_3\text{H}_4\text{Br}_4$, the former boiling at 130°C . (266°F .), the latter decomposing when distilled. With iodine it forms the compound $\text{C}_3\text{H}_4\text{I}_2$, which boils at 198°C . (388.4°F .). It unites with 2 molecules of hydriodic acid, forming the compound $(\text{H}_3-\text{C}-\text{CH}_2-\text{CH}_3)_2$, and similarly with HBr and HCl .

§ *Allylene, or Allene, $\text{CH}_2=\text{C}=\text{CH}_2$* , is formed, as already stated, by the electrolysis of itaconic acid; also by the action of sodium on the modification of dichloropropene obtained from dichlorhydrin (see GUYTON); probably also from allyl iodide. With bromine it forms a crystalline tetrabromide, $\text{C}_3\text{H}_4\text{Br}_4$.

Crotonylene, C_4H_6 or $\text{CH}_3-\text{CH}=\text{C}=\text{CH}_2$, is formed by abstraction of HBr from monobromobutene, $\text{CH}_3-\text{CH}_2-\text{CBr}=\text{CH}_2$, also by distilling orthite, $\text{C}_4\text{H}_{10}\text{O}_4$, with formic acid. It is a liquid boiling at $20-25^\circ\text{C}$. ($68-77^\circ\text{F}$.), and forming a tetrabromide which crystallizes in shining rhombic plates, melting at 116°C . (240.8°F .). It does not form any metallic derivative with copper or silver, whence, and from its mode of formation, it may be referred to the β series.

Valerylene or Pentene, C_5H_8 .—Of this hydrocarbon two modifications are known. a *Valerylene*, probably $\text{HC}=\text{C}=\text{CH}_2$, is formed by abstraction of H_2Cl from methylpropyl-ketonic chloride, $\text{H}_3\text{C}-\text{CCl}_2-\text{C}_2\text{H}_5$. It boils at 50°C . (122°F .), and yields metallic derivatives with silver and copper.

§ *Valerylene*, probably $\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_2\text{C} \end{array} > \text{C}=\text{C}=\text{CH}_2$, is formed by abstraction of HBr from bromisopentene, $\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_2\text{C} \end{array} > \text{C}=\text{CH}-\text{CBr}=\text{CH}_2$. It is a liquid hav-

ing an alliaceous odor, a specific gravity of 0.700, and boiling at 45°C . (113°F .). It does not form compounds with silver and copper. It forms a dibromide which boils at 170°C . (338°F .), and a liquid tetrabromide.

Hexinea, C_6H_{10} .—*Hexylene*, probably $\text{CH}_2-(\text{CH}_2)_3-\text{C}\equiv\text{CH}$, obtained by abstraction of HBr from monobromohexene, boils at $76-80^{\circ}\text{C}$. ($168.8-176^{\circ}\text{F}$.).

Diallyl, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$, is formed by the action of sodium or silver on allyl iodide. It is a volatile, pungent liquid, boiling at 59°C . (138.2°F .), and forming a crystalline tetrabromide and tetrachloride, the former melting at 63°C . (145.4°F .). When shaken with aqueous hypochlorous acid, it forms the compound $\text{C}_6\text{H}_{10}(\text{Cl})(\text{OH})_2$. Heated with concentrated hydriodic acid it yields the compound $\text{C}_6\text{H}_{12}\text{I}_2$ or $\text{H}_3\text{C}-\text{CHI}-\text{CH}_2-\text{CH}_2-\text{CHI}-\text{CH}_3$, as a heavy oily liquid; and on heating this compound with silver acetate, it is converted into the corresponding diacetate, which, when heated with caustic potash, yields the corresponding hexene glycol,



The higher members of the series $\text{C}_n\text{H}_{2n-2}$ are obtained either from the dibromides of the corresponding olefines, or from substitution-products isomeric therewith. Thus heptene, or α -nanthidene, is formed by the action of potash on α -nanthidene dibromide (obtained by treating α -nanthyl with phosphorus pentachloride); rutilene is prepared from diamylene; and the isomeric body decene or decenylene from the dibrominated derivative of the hydrocarbon $\text{C}_{10}\text{H}_{18}$, which exists in petroleum.

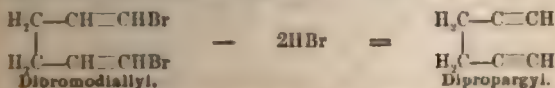
SERIES $\text{C}_n\text{H}_{2n-4}$.

The only known member of the fatty group belonging to this series is valylene or pentone, C_5H_8 , which is formed by the action of alcoholic potash on valerylene dibromide, $\text{C}_5\text{H}_8\text{Br}_2$. It is a light oil, smelling like garlic, and boiling at 50° . It forms precipitates with ammoniacal copper and silver solutions. With bromine in a freezing mixture, it yields a crystalline mass consisting of $\text{C}_5\text{H}_8\text{Br}_6$, saturated with a thick liquid which is a mixture of the same compound with $\text{C}_5\text{H}_8\text{Br}_4$, and probably $\text{C}_5\text{H}_8\text{Br}_2$.

The terpenes, $\text{C}_{10}\text{H}_{16}$, also come under the formula $\text{C}_n\text{H}_{2n-4}$, but they belong rather to the aromatic group.

SERIES $\text{C}_n\text{H}_{2n-6}$.

Dipropargyl, C_6H_6 or $\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$, the only known hydrocarbon of the fatty group belonging to this series, is isomeric with benzene, but differs greatly from that body in its properties. It is prepared by distilling diallyl tetrabromide, $\text{C}_6\text{H}_{10}\text{Br}_4$, with a large excess of caustic potash, whereby it is converted into dibromodiallyl, $\text{C}_6\text{H}_8\text{Br}_2$, and boiling the latter with alcoholic potash:



Dipropargyl is a mobile, limpid, highly refractive liquid, having an intensely pungent odor, a specific gravity of 0.81 at 18°C . (64.4°F .), and

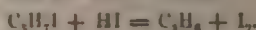
boiling at 85°C . (185°F .). With ammoniacal cuprous chloride it forms a greenish-yellow precipitate, $\text{C}_6\text{H}_5\text{Cu}_2 + 2\text{H}_2\text{O}$, and with silver nitrate, a white precipitate, $\text{C}_6\text{H}_5\text{Ag}_2 + 2\text{H}_2\text{O}$, which blackens on exposure to light and explodes at 100° , leaving carbon and silver.

Dipropargyl is easily distinguished from benzene by its property of combining explosively with bromine, forming the tetrabromide $\text{C}_6\text{H}_2\text{Br}_4$, a viscid liquid, of specific gravity 2.460 at 19°C . (66.2°F .), which combines in the dark with more bromine, forming the octobromide $\text{C}_6\text{H}_2\text{Br}_8$, which boils at 140°C . (284°F .).

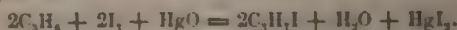
HALOGEN DERIVATIVES OF THE HYDROCARBONS. HALOID ETHERS.

These compounds are formed, as already observed, by substitution of a halogen element (Br, Cl, I) for an equivalent quantity of hydrogen in a hydrocarbon, or of hydroxyl in the corresponding alcohol. They are monatomic, diatomic, triatomic, etc., according as 1, 2, 3, or more atoms of the halogen are thus introduced.

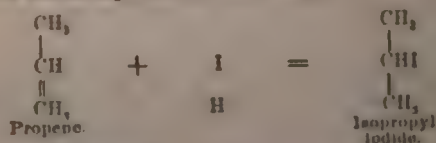
Monatomic Haloid Ethers, $\text{C}_n\text{H}_{2n+1}\text{X}$.—These ethers are derived from the paraffins. Chlorine and bromine act directly on these hydrocarbons, the action of the former being accelerated by light, that of the latter by heat. Iodine likewise acts on the paraffins, removing an atom of hydrogen, and taking its place; but the iodoparaffin thus formed is for the most part reconverted into the original hydrocarbon by the action of the hydriodic acid formed at the same time; thus,



This reverse action may, however, be prevented by the addition of a substance, like mercuric oxide, which decomposes the hydriodic acid as fast as it is formed, and in that case an iodoparaffin or alcoholic iodide is obtained: *e. g.*,



These monatomic haloid ethers are also produced by the action of the haloid compounds of hydrogen and of phosphorus on the corresponding alcohols (*q. v.*), and by addition of a haloid acid to an unsaturated hydrocarbon, *i. e.*, a hydrocarbon in which a pair of carbon-atoms are joined together by two combining units (*p. 504*): *e. g.*,



These ethers are converted—

- a. Into the original paraffins by the action of *nascent hydrogen* (evolved by hydrochloric acid and zinc, or by sodium amalgam):
- b. Into the corresponding alcohols by the action of moist *alcali oxide*.

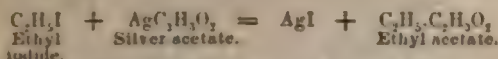


Potassium hydroxide acts in a similar manner, but the resulting alcohol (especially if a secondary alcohol) is partly converted by dehydration into the corresponding olefine, *e. g.*, $\text{C}_3\text{H}_7\text{O} - \text{H}_2\text{O} = \text{C}_3\text{H}_6$.

y. Into oxygen-ethers by the action of the sodium or potassium derivatives of the alcohols; thus,



z. Into compound ethers by the silver salts of the corresponding acids;



The individual ethers of this group will be described in connection with the corresponding alcohols.

Monatomic Haloïd Ethers, $C_2H_{2n-1}X$.

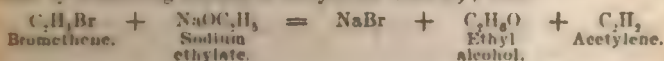
These ethers are derived from the olefines, C_nH_{2n} , by substitution of 1 atom of chlorine, etc., for hydrogen. They cannot, however, be formed by direct substitution, as the action of chlorine, bromine, or iodine on the olefines gives rise to addition-products, $C_nH_{2n}Cl_2$, etc.; but they may be obtained by treating these addition-products with alcoholic potash or silver oxide; thus,



These ethers, like the olefines from which they are derived, can take up 2 atoms of chlorine, bromine, or iodine, forming compounds which can likewise give up hydrochloric, hydrobromic, or hydriodic acid, under the influence of alcoholic potash; the body thus formed can take up 2 atoms of chlorine, bromine, or iodine, then give up HCl, HBr, or HI; and thus, by a series of perfectly similar reactions, we at length arrive at bodies consisting of the primitive olefine with all its hydrogen replaced by chlorine, bromine, or iodine, and the dichlorides, dibromides, and diiodides of these last-mentioned bodies: thus, from ethene may be derived the following series of brominated compounds:

| | | | |
|---------------------------|--------------|-----------------------------------|-------------------|
| Ethene | C_2H_4 | Ethene bromide | $C_2H_4Br_2$ |
| Bromethene | C_2H_3Br | Bromethene bromide | $C_2H_3Br.Br_2$ |
| Dibromethene | $C_2H_2Br_2$ | Dibromethene bromide | $C_2H_2Br_2.Br_2$ |
| Tribromethene | C_2HBr_3 | Tribromethene bromide | $C_2HBr_3.Br_2$ |
| Tetrabromethene | C_2Br_4 | Tetrabromethene bromide | $C_2Br_4.Br_2$ |

Further, a monochlorinated or monobrominated olefine may give up the atom of chlorine or bromine which it contains, in the form of hydrochloric or hydrobromic acid, whereby it is reduced to a hydrocarbon of the series C_nH_{2n-2} . This reaction may take place at 130° – 150° C. (266° – 302° F.), under the influence of alcoholic potash, or, better, of sodium ethylate (obtained by dissolving sodium in anhydrous alcohol); thus:

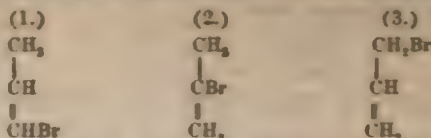


Chlorethene or *Vinyl Chloride*, $C_2H_3Cl = CH_2 \cdot CHCl$ (the univalent radical $CH_2 \cdot CH-$ being called *vinyl*), is a gas having an alliaceous odor, and liquefying at 18° C. (64.4° F.).

Bromethene or *Vinyl Bromide*, C_2H_3Br , smells like the chloride, has a specific gravity of 1.52, and boils at 23° C. (73.4° F.). When kept in sealed tubes, it sometimes solidifies to a white amorphous mass, having the appearance of porcelain.

Iodethene or *Vinyl iodide*, C_2H_3I , has a specific gravity of 1.98, and boils at 55° C. (131° F.).

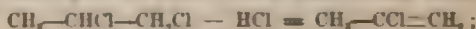
Propene yields three series of monatomic haloid ethers: *a. g.*



1. The only known ether of the first group is the bromide, which liquid boiling at $48^\circ C.$ ($118.4^\circ F.$), produced by addition of hydrobromic acid to allylene:



2. The ethers of the second group, called chloropropene, etc., formed by the action of alcoholic potash on the chloride, etc., of propene, the action consisting in the abstraction of HCl , etc. (p. 515):



also from acetone chloride (p. 519):

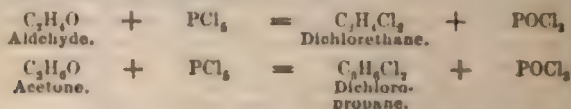


Chloropropene has a specific gravity of 0.918 at $9^\circ C.$ ($48.2^\circ F.$), and at $23^\circ C.$ ($73.4^\circ F.$). *Bromopropene* has a specific gravity of 1.411 at $10^\circ C.$ ($50^\circ F.$), and boils at $57.6^\circ C.$ ($135.7^\circ F.$). It unites directly with hydrogen bromide, forming propene bromide, $CH_3-CHBr-CH_2Br$, and propene bromide, $CH_3-CBr_2-CH_3$.

3. The ethers of the third group, called allyl ethers, are analogous in constitution to allyl alcohol, $CH_2OH-CH=CH_2$, and will be described in connection therewith.

Diatomic Haloid Ethers, $C_nH_mX_r$.

These ethers are formed: 1. From the paraffins, by direct substitution of Cl, Br , etc., for H . 2. From the olefines, C_nH_{2n} , by direct addition of Cl_2 , etc. 3. By the action of the chlorides, bromides, and iodides of phosphorus on aldehydes and ketones; thus,

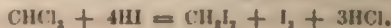


Methane Derivatives.—*Dichloromethane*, CH_2Cl_2 , is formed by chlorination of methyl chloride, CH_3Cl ; and by the action of chlorine on di-iodomethane or on methyl iodide:



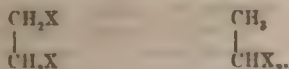
It is a colorless liquid, having a specific gravity of 1.36 at 0° , and boiling at $40^\circ C.$ ($104^\circ F.$).

Di-iodomethane, CH_2I_2 , is produced by heating trichloro- or tetrachloromethane to $130^\circ C.$ ($266^\circ F.$) with fuming hydriodic acid:

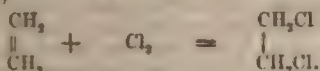


It crystallizes in colorless shining laminae of specific gravity 3.34 at 0° , melts at 6° C. (42.8 F.), and boils at 182° C. (359.6 F.).

Ethane Derivatives, $C_2H_4X_2$.—These ethers admit of two modifications, accordingly as the two atoms of the chlorous radicle X are attached to different atoms, or to the same atom of carbon; thus



The ethers of the first modification are formed by direct addition of chlorine, bromine, or iodine, to ethene; the double linking of the two carbon-atoms in the molecule of free ethene being loosened by the entrance of two chlorine-atoms into the group, and the ethene then becoming a valent radicle; thus,



These ethers are accordingly regarded as chloride, bromide, or iodide of ethene.

The ethers of the second modification are produced by the action of the perchloride, etc., of phosphorus on aldehyde, the reaction consisting in the placement of the oxygen atom of this compound by 2 atoms of chlorine, e. g.,



They may be supposed to contain the bivalent radicle ethidene, CH_2-CH_2 ; but this radicle has not been isolated.

Ethene Chloride, $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{CH}_2\text{Cl} \end{array}$.—This compound has

long been known by the name of *Dutch liquid*, having been discovered by four Dutch chemists in 1795. When equal measures of ethene gas and chlorine are mixed over water, absorption of the mixture takes place, and a yellowish oily liquid is produced, which collects upon the surface of the water, and ultimately sinks to the bottom in drops. It may be easily prepared, in quantity, by causing the two gases to combine in a glass globe (fig. 172) having a narrow neck at the lower part, dipping into a small bottle, to receive the product. The two gases are conveyed by separate tubes, and allowed to mix in the globe, the ethene gas being kept a little in excess. The chlorine should be washed with water, and the ethene passed through strong oil of vitriol, to remove vapor of ether: the presence of sulphuric acid and carbonic acids is not injurious. Combination takes place very rapidly, and the liquid product slides down the sides of the globe into the receiver. When a considerable quantity has been collected, it is agitated, first with water, and afterwards with concentrated sulphuric acid, and, lastly, purified by distillation.

Fig. 172.



Pure ethene chloride is a thin, colorless liquid, of fragrant odor and sweet taste: it is slightly soluble in water, and readily so in alcohol and ether. It has a specific gravity 1.271 at $0^\circ C$, and boils at $85^\circ C$. ($185^\circ F$). It is unaffected by oil of vitriol or solid potassium hydrate. When inflamed it burns with a greenish, smoky light. When treated with an alcoholic solution of potash, it is slowly resolved into potassium chloride, which separates, and chloroethene, C_2H_3Cl , whose vapor requires to be cooled down to $-18^\circ C$. ($-0.4^\circ F$.) before it condenses; at this temperature it forms a limpid, colorless liquid. Chlorine is absorbed by this latter substance, and a compound is produced, which contains $C_2H_2Cl_2$, and this is in turn decomposed by an alcoholic solution of potash into potassium chloride and another volatile liquid, $C_2H_2Cl_2$. This series of reactions is analogous to that already noticed in the case of the bromine compounds (p. 515).

Ethidene Chloride, CH_3-CHCl_2 , is best prepared by the action of phosphoric chloride on aldehyde: it is also formed by the action of chlorine on ethyl chloride. It is a colorless liquid smelling like chloroform, having a specific gravity of 1.198, and boiling at $58^\circ C$. ($136.4-138.2^\circ F$.). When subjected to the action of chlorine, it yields the compounds $CH_3.CCl_2$ and $CH_2Cl.CHCl_2$, together with other products.

Ethene Bromide, CH_2Br-CH_2Br , obtained by saturating bromine with olefiant gas, is an oily fragrant liquid, of specific gravity 2.163 at $21^\circ C$. ($69.8^\circ F$.), boiling at $129^\circ C$. ($264.2^\circ F$.), and solidifying at 0° to a crystalline mass which melts at $9^\circ C$. ($48.2^\circ F$.).

Ethidene Bromide, CH_3-CHBr_2 , obtained similarly to the chloride, is a liquid boiling at $110-114^\circ C$. ($230-237.2^\circ F$.), and decomposing when heated with water.

These two bromides are also formed by heating monobromethene, $CH_2=CHBr$, with hydrobromic acid, the ethene compound when the acid is highly concentrated, the ethidene compound when it is more dilute.

Ethene Iodide, CH_2I-CH_2I , is produced by the direct combination of iodine with ethene in sunshine or under the influence of heat, also by passing ethene gas into an alcoholic solution of iodine. It crystallizes from alcohol in shining needles, melts at $73^\circ C$. ($163.4^\circ F$.), and decomposes at higher temperatures into ethene and iodine.

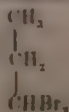
Ethidene Iodide, CH_3I-CHI_2 , is obtained by heating the chloride with aluminum iodide:—



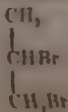
also by addition of hydriodic acid to acetylene: $C_2H_2 + 2HI = C_2H_4I_2$. It is a liquid having a specific gravity of 2.84 at 0° , and boiling at $175^\circ C$. ($352.4^\circ F$.).

Propane Derivatives, C_3H_7X .—The diatomic ethers derived from propane admit of four modifications, as exhibited by the following formulae of the bromide:—

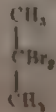
1. Propylene bromide.



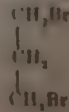
2. Propene bromide.



3. Methylbromacetol.



4. Trimethene bromide.

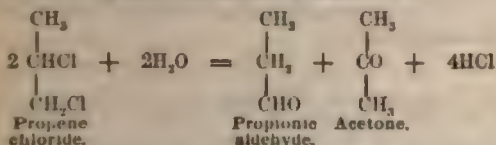


The propidene or propylidene ethers are formed by the action of phosphorus pentachloride, etc., on propylic aldehyde, CH_3-CH_2-CHO . *Propidene* is a liquid having an alliaceous odor, and boiling at $84-87^\circ C.$ ($183-189^\circ F.$). The bromide and iodide are not known.

The propene or propylene ethers are formed by direct combination of propene with chlorine, bromine, and iodine. When treated with silver oxide and water they are converted into propene alcohol or propylene glycol, $CH_2-CHOH-CH_2OH$.

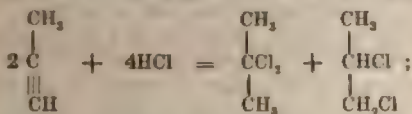
Propene chloride, $CH_3-CHCl-CH_2Cl$, is also formed by the action of chlorine on propene in sunshine and in presence of iodine, on pseudopropyl chloride, $-CHCl-CH_3$. If iodine is not present, acetone chloride is formed at the same time. Propene chloride has a specific gravity of 1.165 at $14^\circ C.$ ($57.2^\circ F.$), and boils at $98^\circ C.$ ($208.4^\circ F.$). The *bromide*, formed by direct combination or by the action of bromine on pseudopropyl bromide, is a liquid of specific gravity 1.946 at $17^\circ C.$ ($62.6^\circ F.$), and boiling at $142^\circ C.$ ($287.6^\circ F.$). The *iodide*, produced by direct combination of propene with iodine at $50^\circ C.$ ($122^\circ F.$), is a colorless oil not distillable without decomposition.

Propene chloride or bromide of propene heated with water at $200^\circ C.$ ($392^\circ F.$) is converted into propionic aldehyde and acetone:—



The propene derivatives of the form $CH_3-CX_2-CH_3$, are produced by substitution of Cl_2 or Br_2 for O , the substitution being effected by the action of PCl_5 or PBr_5 .

Acetone chloride, or *Methylchloroacetol*, $CH_3-CCl_2-CH_3$, is also produced, together with propene chloride, by addition of HCl to allylene, C_3H_4 , thus:



Acetone chloride of pseudopropyl chloride. It is a colorless liquid of specific gravity 1.827 at $16^\circ C.$ ($60.8^\circ F.$), and boiling at $70^\circ C.$ ($158^\circ F.$). Sodium reduces it to ordinary propene. With alcoholic potash it is converted into chloropropene, $CH_2=CH-CH_2Cl$, which is also formed in the same way from propene dichloride. Heated to $150^\circ C.$ ($302^\circ F.$) with water, it is partially converted into acetone.

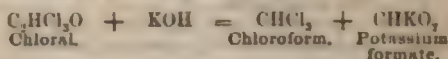
Trimethene Bromide, $CH_2Br-CH=CH_2Br$, is formed by heating allyl alcohol, $CH_2=CH-CH_2OH$, with hydrobromic acid; also, together with propene bromide, by heating allyl bromide to 100° with hydrobromic acid.

It is a colorless liquid, of specific gravity 1.93 at $19^\circ C.$ ($66.2^\circ F.$), boiling at $162^\circ C.$ ($323.6^\circ F.$); converted by alcoholic potash into allyl bromide and allyl-ethyl oxide, $CH_2=CH-CH_2-O-C_2H_5$.

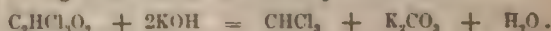
Trimethene chloride, $CH_2Cl-CH=CH_2Cl$, formed by heating the bromide to $160^\circ C.$ ($326.2^\circ F.$) with mercuric chloride, is a fragrant liquid of specific gravity 1.201 at $15^\circ C.$ ($59^\circ F.$), boiling at $117^\circ C.$ ($243^\circ F.$); converted by alcoholic potash into allyl-ethyl oxide.

Triatomic Haloid Ethers, C_nH_{2n-1}X₃.

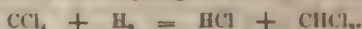
Methenyl Chloride or Chloroform, CHCl₃.—This compound is produced: 1. Together with methane chloride, CH₃Cl, when a mixture of chlorine and gaseous methyl chloride is exposed to the sun's rays. 2. By the action of alkalis on chloral (trichloraldehyde):—



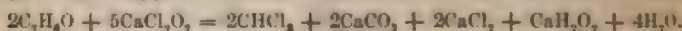
3. By boiling trichloroacetic acid with aqueous alkalis:—



4. By the action of nascent hydrogen on carbon tetrachloride:—

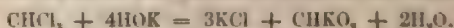


5. By the action of hypochlorites, or of chlorine in presence of alkalis, on various organic substances, as methyl-, ethyl-, and amyl-alcohols, acetic acid, acetone, etc. The reaction is complicated, giving rise to several other products: with common alcohol and calcium hypochlorite the principal reaction appears to be—



Chloroform is prepared on the large scale by cautiously distilling together good commercial chloride of lime, water, and alcohol. The whole product distils over with the first portions of water, so that the operation may be soon interrupted with advantage. The chloroform, which constitutes the oily portion of the distillate, is purified by agitation with water, desiccation with calcium chloride, and distillation in a water-bath.

Chloroform is a thin colorless liquid of agreeable ethereal odor, much resembling that of Dutch liquid, and of a sweetish taste. Its density is 1.525 at 0°, and it boils at 61° C. (141.8 F.): the density of its vapor (compared with air) is 4.20. Chloroform is difficult to kindle, and burns with a greenish flame. It is nearly insoluble in water, and is not affected by concentrated sulphuric acid. When boiled with aqueous potash in a closed tube, it is converted into potassium chloride and formate:—



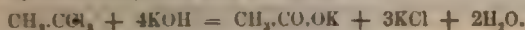
Chloroform is well known for its remarkable effects upon the animal system in producing temporary insensibility to pain when its vapor is inhaled.

Bromoform, CHBr₃, is a heavy, volatile liquid, prepared by the simultaneous action of bromine and aqueous alkalis on alcohol, wood-spirit, and acetone. It has a density of 2.9 at 12° C. (53.6° F.), solidifies at —93° C. (15.8° F.), and boils at 150–152° C. (302–305.6° F.). It is converted by caustic potash into potassium bromide and formate.

Iodoform, CHI₃, is a solid, yellow, crystallizable substance, easily obtained by adding alcoholic solution of potash to tincture of iodine, avoiding excess, evaporating the whole to dryness, and treating the residue with water. It melts at 119° C. (246.2° F.), and distils with vapor of water. It is nearly insoluble in water, but dissolves in alcohol, and is decomposed by alkalis in the same manner as the preceding compounds. Bromine converts it into bromiiodoform, CHBr₂I, a colorless liquid which solidifies at 0°. Iodoform distilled with phosphorus pentachloride

or mercuric chloride, is converted into chloriodoform, CHCl_2I , a colorless liquid of specific gravity 1.96, which does not solidify at any temperature.

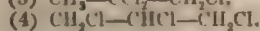
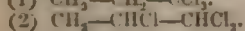
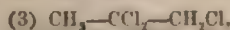
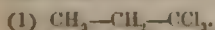
Trichlorethane, $\text{C}_2\text{H}_3\text{Cl}_3$, admits of two modifications, viz.: (1) $\text{CH}_3-\text{CHCl}_2$, formed by the action of chlorine in sunshine on ethyl chloride. It is a liquid smelling like chloroform, boiling at 74.5°C . (167.9°F .), and converted by alcoholic potash into acetic acid:—



(2) $\text{CH}_2\text{Cl}-\text{CHCl}_2$, obtained by the action of chlorine on vinyl chloride, $\text{H}_2\text{C}=\text{CHCl}$ (see VINYL ALCOHOL). It boils at 115°C . (239°F .), and has a specific gravity of 1.422 at 0° . Alcoholic potash solution converts it into dichlorethane, $\text{C}_2\text{H}_4\text{Cl}_2$.

Tribromomethane, $\text{C}_2\text{H}_3\text{Br}_3$, is obtained by adding bromine to bromethene, $\text{C}_2\text{H}_2\text{Br}$, cooled by a freezing mixture. It is a colorless liquid, which smells like chloroform, has a specific gravity of 2.620 at 23°C . (73.4°F .), and boils at 186.5°C . (367.7°F .). Alcoholic potash abstracts HBr , converting it into dibromomethene, $\text{C}_2\text{H}_2\text{Br}_2$.

Trichloropropane, $\text{C}_3\text{H}_5\text{Cl}_3$, admits of four modifications, represented by the following formulae:—

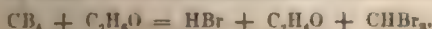


The last of these, which is the most important, is analogous in composition to glycerin, $\text{C}_3\text{H}_5(\text{OH})_3$, and will be described, together with the corresponding bromine- and iodine-derivatives, in connection with that compound.

Haloid Ethers of Higher Orders.

Tetrachloromethane, or **Carbon Tetrachloride**, CCl_4 , is formed by passing the vapor of carbon bisulphide, together with chlorine, through a red-hot porcelain tube. A mixture of sulphur chloride and carbon tetrachloride is formed, which is distilled with potash, whereby the chloride of sulphur is decomposed, and pure carbon tetrachloride passes over. It is a colorless liquid of 1.56 specific gravity, and boils at 77°C . (170.6°F .). The same compound is formed by exhausting the action of chlorine upon marsh-gas or methyl chloride in sunshine. An alcoholic solution of potash converts it into a mixture of potassium chloride and carbonate.

Tetrabromomethane, or **Carbon Tetrabromide**, CBr_4 , is formed by the action of bromine, in presence of iodine bromide or antimonious bromide, on carbon sulphide, bromopierin, bromoform, or chloroform. It is a white crystalline substance, having a specific gravity of 3.42 at 14°C . (57.2°F .), melts at 91°C . (195.8°F .), and boils with slight decomposition at 189.5°C . (373.1°F .). Heated to 100° with alcohol in a sealed tube, it yields hydrogen bromide, aldehyde, and bromoform:—

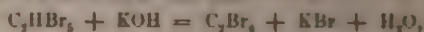


Tetra-iodomethane, or **Carbon Tetra-iodide**, CI_4 , is produced by heating tetrachlorethane with iodide of aluminium. It crystallizes from

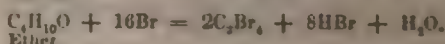
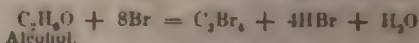
ether in dark-red regular octahedrons of specific gravity 4.32 at 26° (68° F.), and decomposes on exposure to the air, especially at high temperatures, yielding iodine and carbon dioxide.

Tetrabromethane, $C_2H_2Br_4$, formed by direct combination of benzene with dibromomethane, $C_2H_2Br_2$, or with acetylene, C_2H_2 , is a liquid having a specific gravity of 2.88 at 22° C. (71.6° F.), boiling at 200° C. (392° F.) and solidifying in a freezing mixture to a white crystalline mass. By heating with alcoholic potash it is converted into tribromomethane, $CHBr_3$.

Tetrabromethene, or Carbon Dibromide, C_2Br_4 , is formed by the action of alcoholic potash on pentabromomethane:—



or by treating common alcohol or ether with bromine:—



It crystallizes in white plates, melts at 50° C. (120.2° F.), and sublimes without alteration.

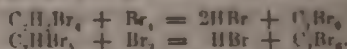
Tetrachlorethene, or Carbon Dichloride, C_2Cl_4 , obtained by passing the vapor of the trichloride or tetrachloride through a red-hot tube, either alone or mixed with hydrogen, or by the action of nascent hydrogen (zinc and dilute sulphuric acid) on the trichloride, is a mobile liquid of specific gravity 1.629, boiling at 117° C. (242.6° F.). When heated to 200° C. (392° F.) with potassium hydroxide, it is completely converted into potassium chloride and oxalate, with evolution of hydrogen:



It absorbs chlorine and bromine in sunshine, forming in the one case the trichloride, C_2Cl_6 , and in the other the chlorobromide, $C_2Cl_3Br_3$.

Pentabromomethene, C_2HBr_5 , obtained by slowly distilling tribromomethene, C_2HBr_3 , with bromine, or by the action of bromine on acetylene, crystallizes from alcohol in prisms smelling like camphor, melting at 45-50° C. (120.2-122° F.), and decomposed by distillation.

Hexbromomethene, or Carbon Tribromide, C_2Br_6 , is formed by heating the dibromide with bromine in a sealed tube, or by heating either of the compounds, $C_2H_2Br_4$, C_2HBr_3 , with bromine in a sealed tube:



This compound dissolves sparingly in alcohol or ether, easily in carbon sulphide, from which it separates on evaporation in hard, rather thick rectangular prisms. At 200-210° C. (392-410° F.) it melts and decomposes, yielding carbon dibromide and free bromine.

Hexchlorethane, or Carbon Trichloride, $C_2Cl_6 = (CCl_3)_2$, is the final product of the action of chlorine in sunshine on ethyl chloride, C_2H_5Cl , or ethene chloride, $C_2H_4Cl_2$. It is a white, crystalline substance,

aromatic odor, insoluble in water, but easily dissolved by alcohol and ether. It melts at 160° C. (320° F.), and boils at 182° C. (359.6° F.). It burns with difficulty, and is not altered by distillation with aqueous or alcoholic potash. Its vapor, passed through a red-hot porcelain tube filled with fragments of glass or rock-crystal, is decomposed into free chlorine, the dichloride, C_2Cl_4 .

Tetrachlorodibromethane, or Carbon Chlorobromide, $C_2Cl_4Br_2$, is formed by the action of bromine in sunshine on the dichloride, C_2Cl_4 , is a white crystalline body resembling the trichloride.

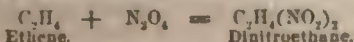
Carbon monochloride, C_2Cl_2 , analogous to ethine or acetylene, is formed by passing the vapor of chloroform or of carbon-dichloride through a red-hot tube. It forms white needles, subliming between 175° and 200° ($347-392^{\circ}$ F.).

NITROPARAFFINS, $C_nH_{2n+1}(NO_2)$.

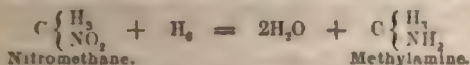
These compounds, isomeric with the nitrous ethers of the fatty series, are produced, together with the latter, by the action of silver nitrite on iodoparaffins or alcoholic iodides,—nitromethane, for example, from methyl iodide :



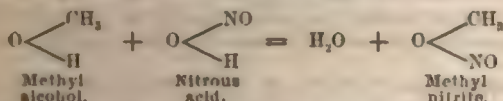
They are also formed by the action of nitrogen tetroxide, or of fuming nitric acid, on the hydrocarbons of the ethene series ;



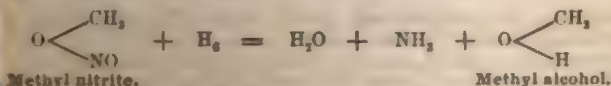
They have their nitrogen-atom in direct union with a carbon-atom, and are consequently converted by nascent hydrogen (evolved from water by zinc-amalgam) into amidoparaffins or amines ; e. g.,



The nitrous ethers, on the other hand, which are formed by the action of nitrous acid on the corresponding alcohols, have their nitrogen united to carbon, only through the medium of oxygen ; e. g.,



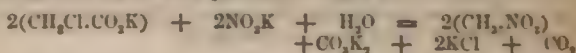
They are accordingly converted by nascent hydrogen into ammonia and the corresponding alcohols ; e. g.,



The nitroparaffins are mostly decomposed, with explosion, when rapidly heated. They are not decomposed by potash or soda, whereas the nitrous

ethers are quickly resolved thereby into nitrous acid and the corresponding alcohols.

Nitromethane, CH_3NO_2 , is formed, as above stated, by the action of silver nitrite on methyl iodide. The action is very violent, and the whole of the methyl iodide is converted into nitromethane, without a trace of the isomeric methyl nitrite. It is also formed by heating the potassium salt of monochloroacetic acid with potassium nitrite:



Nitromethane is a heavy oil, having a peculiar odor, and boiling at $96-101^\circ$. When treated with an alcoholic solution of soda, it yields transparent needles of the sodium derivative, $\text{CH}_2\text{Na}(\text{NO}_2)$, the aqueous solution of which gives characteristic precipitates with various metallic solutions.

Bromonitromethane, $\text{CH}_2\text{Br.NO}_2$, formed by the action of bromine on the dry sodium compound, is a heavy, pungent, strongly refracting liquid, boiling at $143-144^\circ$ C. ($289-291.2^\circ$ F.).

Nitroethane, $\text{C}_2\text{H}_5\text{NO}_2 = \text{CH}_3-\text{CH}_2-\text{NO}_2$, prepared like the methane-derivative, is a colorless, strongly refracting liquid, having a fragrant etheral odor, a specific gravity = 1.0582 at 13° C. (55.4° F.), and boiling at $111-113^\circ$ C. ($231.8-235.4^\circ$ F.): ethyl nitrite boils at 16° C. (60.8° F.). The vapor is inflammable, and burns with a pale yellow flame, but does not explode, even when heated above its boiling point. By nascent hydrogen it is converted into amidethane or ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$.

Bromonitroethane, $\text{C}_2\text{H}_4\text{Br.NO}_2$, and **dibromonitroethane**, $\text{C}_2\text{H}_3\text{Br}_2(\text{NO}_2)$, are formed by the action of bromine on sodium-nitroethane. The former is a heavy acid oil, boiling at $145-146^\circ$ C. ($293-298.4^\circ$ F.), the latter a mobile neutral liquid, boiling at $162-164^\circ$ C. ($323.6-327.2^\circ$ F.).

Nitropropanes, $\text{C}_3\text{H}_7\text{NO}_2$.—There are two isomeric bodies having this composition, obtained by the action of silver nitrite on the iodides of normal propyl and pseudopropyl respectively.

Nitropropane, $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{NO}_2$, is a limpid mobile liquid, very little heavier than water, and boiling at $122-127^\circ$ C. ($251.6-260.6^\circ$ F.).

Pseudo-nitropropane, $\text{H}_3\text{C} > \text{CH}-\text{NO}_2$, boils at $112-117^\circ$ C. ($233.6-242.6^\circ$ F.). Both form crystalline sodium compounds.

Nitro-isobutane, $\text{C}_4\text{H}_9\text{NO}_2 = \text{H}_3\text{C} > \text{CH}-\text{CH}_2-\text{NO}_2$, from isobutyl iodide, is an oil smelling like peppermint, boiling at $135-140^\circ$ C. ($275-284^\circ$ F.) and converted by nascent hydrogen into isobutylamine.

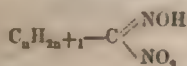
Nitro-isopentane, $\text{C}_5\text{H}_{11}\text{NO}_2 = \text{H}_3\text{C} > \text{CH}-\text{CH}_2-\text{CH}_2-\text{NO}_2$, formed by the action of silver nitrite on ordinary amyl iodide, boils at $155-160^\circ$ C. ($311-320^\circ$ F.).

Reactions of Nitroparaffins with Metallic Salts.—The following table exhibits the reactions of various metallic salts with the sodium compounds of nitromethane, nitroethane, and the two nitropropanes, which are sufficiently characteristic to be used for distinguishing these compounds one from the other.

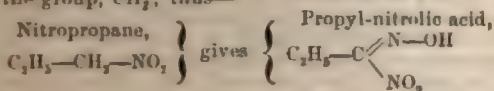
| | Sodium-derivative of | | | |
|------------------------|---|--|---|---|
| | Nitromethane. | Nitro-ethane. | Nitropropane. | Pseudonitropropane. |
| Mercuric
chloride. | Light yellow precipitate; explosive. | White crystalline precipitate. | White crystalline precipitate. | White crystalline precipitate. |
| Mercurous
chloride. | Black flocculent precipitate. | Dirty-gray precipitate. | Black flocculent precipitate. | Black flocculent precipitate. |
| Mercuric
iodide. | Dark brownish-red precipitate. | Blood-red coloration. | Blood-red solution. | Blood-red solution. |
| Mercuric
nitrate. | Grass-green precipitate. | Deep-green solution. | Deep-green solution. | Deep-green solution. |
| Mercuric
acetate. | White precipitate. | 0 | White precipitate. | 0 |
| Mercuric
nitrate. | White precipitate, almost immediately turning black | White precipitate, soon turning brown. | White precipitate, gradually turning brown. | Light yellow precipitate, soon turning black. |

Reaction of Nitrous Acid on the Nitroparaffins.—The reactions of these bodies with nitrous acid (or better, with potassium nitrite and sulphuric acid) are considerably, according as they contain primary, secondary, or tertiary alcohol-radicles (p. 496).

Treating the nitro-compounds of the primary alcohol radicles, in which the NO_2 -group is united to the group CH_2 , with potassium nitrite and dilute sulphuric acid, the solution acquires a deep-red color, and compounds called nitrolic acids, having the general formula—

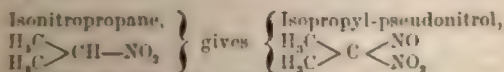


is produced by substitution of nitrosyl, NO , for one of the hydrogen-atoms in the group, CH_2 ; thus—



Nitrolic acids are colorless, crystalline bodies, soluble in ether. Their alkali-salts have a deep-red color: hence the red tint produced at the commencement of the reaction above mentioned, and disappearing when the hydrazine acid is added in excess.

The nitro-compounds of the secondary alcohol-radicles, in which the nitro-group is linked to the group CH , give, when similarly treated, deep-blue solutions, which after a while deposit colorless compounds called pseudonitrols; e. g.—



These compounds are colorless in the solid state, dark-blue in the fused state or in solution.

The nitro-compounds of the tertiary alcohol-radicles, in which the NO_2 -group is associated only with carbon: *e. g.*, $(\text{CH}_3)_3\text{C}\cdot\text{NO}_2$, are neither decomposed nor colored by nitrous acid.

These reactions afford a characteristic and delicate test for distinguishing the primary, secondary, and tertiary alcohol-radicles (in their iodides) from one another.

Nitroparaffins of Higher Orders.

Trinitromethane, or Nitroform, $\text{CH}(\text{NO}_2)_3$, is produced by the action of nitric acid on various organic compounds, but is most conveniently obtained as an ammonium salt, $\text{C}(\text{NO}_2)_3\cdot\text{NH}_4$, by the action of water or alcohol on trinitracetonitril or cyanotrinitro-methane: $\text{C}(\text{NO}_2)_3\text{CN} + 2\text{H}_2\text{O} = \text{C}(\text{NO}_2)_3\text{NH}_4 + \text{CO}_2$; and on treating the yellow crystalline salt thus formed with strong sulphuric acid, nitroform is obtained in the free state.

Nitroform, at temperatures above 15°C . (59°F .), is a colorless oil; below that temperature it solidifies in colorless cubic crystals. It is moderately soluble in water, forming a dark yellow solution. It cannot be distilled, as it explodes with violence when heated.

The atom of hydrogen in nitroform may be replaced either by metals or by chlorous radicles, namely, bromine and nityl. The metallic derivatives or *salts of nitroform*, are for the most part yellow and crystallizable: they explode when heated.

Bromonitroform, $\text{C}(\text{NO}_2)_3\text{Br}$, produced by exposing nitroform to the action of bromine for some days under the influence of direct sunshine, or more easily by treating an aqueous solution of mercuric nitroform, $\text{C}_4(\text{NO}_2)_4\text{Hg}$, with bromine, is a colorless liquid above 12°C . (53.6°F .), but solidifies below that temperature to a white crystalline mass. It is somewhat soluble in water, and may be distilled with aqueous vapor, or in a current of air. It decomposes at 140°C . (284°F .).

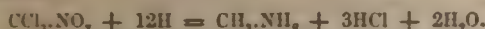
Tetranitromethane, $\text{C}(\text{NO}_2)_4$, is produced by treating nitroform with fuming nitric and sulphuric acids, heating the liquid to 100° , and passing air through it. A liquid then distils over, from which water throws down tetranitromethane as a heavy oil.

Tetranitromethane is liquid at ordinary temperatures, but solidifies at 13°C . (55.4°F .) to a white crystalline mass. It is insoluble in water, but soluble in alcohol and ether. It boils at 126°C . (258.8°F .), and unlike nitroform, may be distilled without decomposition. When quickly heated it decomposes, with evolution of nitrous vapors, but without explosion. It does not take fire by contact with flame, but a glowing coal on which it is poured burns with a bright light.

Nitrotrichloromethane, Nitrochloroform or Chloropicrin, $\text{C}(\text{NO}_2)\text{Cl}_3$, is produced by the action of nitric acid on various chlorinated organic compounds—chloral, for example; also by that of chlorine or hypochlorites on nitro-compounds, such as fulminating silver, $\text{C}_2\text{N}_2\text{O}_2\text{Ag}_2$, and picric acid, $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{O}$. To prepare it, 10 parts of freshly prepared bleaching powder, made into a thick paste with water, are introduced into a retort, and a saturated solution of 1 part of picric acid heated to 30°C . (86°F .) is added. Reaction then generally takes place, without further heating, and the chloropicrin distils over with vapor of water.

Chloropicrin is a colorless liquid, having a specific gravity of 1.665, and boiling at 112°C . (233.6°F .). It has a very pungent odor, and explodes when suddenly heated. By the action of nascent hydrogen (evolved by

tion of iron on acetic acid) it is reduced to amidomethane or ethylamine:

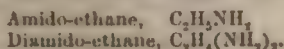


Picropicrin, $\text{C}(\text{NO}_2)\text{Br}_3$, is formed in like manner by heating picric acid with calcium hypobromite (slaked lime and bromine). It closely resembles chloropicrin, solidifies below 10°C . (50°F .); and may be distilled in vacuum without decomposition.

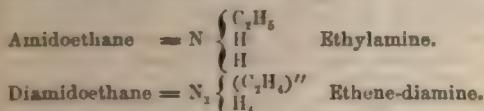
Dichloromethane, $\text{C}(\text{NO}_2)_2\text{Cl}_2$ (commonly called *Marignac's* oil) is obtained by distilling chloronaphthalene with nitric acid, is very like chloropicrin.

AMIDOPARAFFINS.

They are derivatives formed by the replacement of 1, 2, or more hydrogens in a paraffin by the monatomic radicle amidogen, NH_2 ; e. g.,



They are volatile and strongly basic compounds, exhibiting in their behavior with acids and other bodies the closest resemblance to ammonia: they indeed be regarded as derived from one or more molecules of ammonia by the substitution of alcohol-radicles, mono- or polyatomic, for equivalent quantities of hydrogen: hence they are called amines; e. g.,

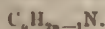


mono-derivatives are formed by the action of reducing agents on the Nitroparaffins: nitroethane, for example, treated with iron and acetic acid, is converted into ethylamine:—



They are more readily prepared by other methods, which, together with the properties and reactions of these bodies, will be discussed in a chapter.

AZOPARAFFINS, NITRILS, or CYANIDES,



These compounds may be regarded as derived from the paraffins by substitution of trivalent nitrogen for 3 atoms of hydrogen, or as compounds containing trivalent radicles, $\text{C}_n\text{H}_{2n-1}$ (nitrils), or as compounds containing a univalent radicle, $\text{N}\equiv\text{C}-$ (cyanogen) with a univalent radicle $\text{C}_n\text{H}_{2n+1}$; e. g.,

* If $n-1=p$, $2n-1=2p+1$.

which gives $2 \times 12 + 2 \times 14 = 52$.

The univalent radicle CN is often represented by the shorter fo

In the preparation of cyanogen from mercuric cyanide, a br
blackish substance, called paracyanogen, is always forme
quantity. It is insoluble in water, and when calcined in a gas
not act upon it, such as nitrogen or carbon dioxide, is complet
ized in the form of cyanogen gas, without leaving any carbon
due: hence it appears to be isomeric or polymeric with cyanogen

Hydrogen Cyanide; Hydrocyanic or Prussic
HCN.—This very important compound, so remarkable for its
properties, was discovered as early as 1782 by Scheele.

Pure anhydrous hydrocyanic acid may be obtained by passin
phuretted hydrogen gas over dry mercuric cyanide, gently heated
tube connected with a small receiver cooled by a freezing mixtu
a thin, colorless, and exceedingly volatile liquid, which has a
0.7058 at 7.2°C . (45°F .), boils at 26.1°C . (80°F .), and solid
cooled to -18°C . (0.5°F .): its odor is very powerful and most
istic, much resembling that of peach-blossoms or bitter almond
a very feeble acid reaction, and mixes with water and alcohol
portions. In the anhydrous state this substance constitutes
most formidable poisons known, and even when largely diluted
its effects upon the animal system are exceedingly energetic;
ployed, however, in medicine, in very small doses. The inhale
vapor should be carefully avoided in all experiments in which hy
acid is concerned, as it produces headache, giddiness, and other
able symptoms; ammonia and chlorine are the best antidotes.

The acid in its pure form can scarcely be preserved; even wh
in a carefully stoppered bottle, it is observed after a very sho
darken, and eventually to deposit a black substance containi
nitrogen, and perhaps hydrogen: ammonia is formed at the same
many other products. Light favors this decomposition. Even
lute state it is apt to decompose, becoming brown and turbid

A solution of hydrocyanic acid may be prepared by various means. It is economical, and by far the best, where considerable quantities are required, is to decompose yellow potassium ferrocyanide at boiling heat with sulphuric acid. 500 grains of the powdered ferrocyanide, are dissolved in four or five ounces of warm water, and introduced into a capacious flask or globe, connected by a perforated cork and a tube with a Liebig's condenser well supplied with cold water; 10 lbs. of oil of vitriol are diluted with three or four times as much water and added to the contents of the flask; and the distillation is carried on until about half the liquid has distilled over, after which the process is interrupted. The residue in the retort is a white or yellow mass, consisting of potassio-ferrous ferrocyanide, $K_2Fe''Cy_6$ (see p. 534), mixed with potassium sulphate.



When hydrocyanic acid is wanted for the purposes of pharmacy, it is prepared as a strong solution in the manner above described, and then, after ascertaining its exact strength, to dilute it with pure water to the strength of the Pharmacopœia, viz., 2 per cent. of real acid. This examination is best made by precipitating with excess of silver nitrate a weight of the acid to be tried, collecting the insoluble silver cyanide on a small filter previously weighed, then washing, drying, and lastly, weighing the whole. From the weight of the cyanide that of the hydrocyanic acid can be easily calculated, a molecule of the one ($CNAg = 134$), adding with a molecule of the other ($CNH = 27$); or the weight of the silver cyanide may be divided by 5, which will give a close approximation to the truth.

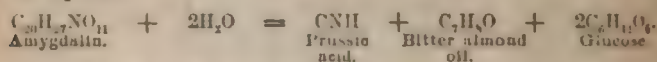
A very good method for determining the amount of hydrocyanic acid in a liquid has been suggested by Liebig. It is based upon the process suggested by potassium cyanide of dissolving a quantity of silver sufficient to produce with it a double cyanide, $KCy.AgCy$. Hence a solution of hydrocyanic acid, which is supersaturated with potash, and to which a few drops of solution of common salt, will not yield a precipitate with silver nitrate before the whole of the hydrocyanic acid is converted into the above double salt. If we know the amount of silver in a given volume of the nitrate solution, it is easy to calculate the amount of hydrocyanic acid; for this quantity will stand to the amount of silver in the nitrate consumed, as 2 molecules of hydrocyanic acid to 1 molecule of silver, *i. e.*:

$$108 : 54 = \text{silver consumed} : x.$$

A common remark, that the hydrocyanic acid made from potassium ferrocyanide keeps better than that made by other means. The cause of its stability is ascribed to the presence of a trace of mineral acid. Everitt found that 10 drops of hydrochloric acid, added to a large bulk of the pure acid, preserved it from decomposition, while another portion, not so treated, became completely spoiled.

A convenient process for the extemporaneous preparation of an acid of definite strength, is to decompose a known quantity of potassium ferrocyanide with solution of tartaric acid: 100 grains of crystallized tartaric acid powder, 44 grains of potassium cyanide, and 2 measured ounces of water, shaken up in a phial for a few seconds, and then left at rest until the precipitate may subside, will yield an acid of very nearly the required strength. A little alcohol may be added to complete the solution of the cream of tartar; no filtration or other treatment need be applied.

Bitter almonds, the kernels of plums and peaches, the seeds of the apple, the leaves of the cherry-laurel, and various other parts of plants belonging to the great natural order *Rosaceæ*, yield on distillation with water a sweet-smelling liquid containing hydrocyanic acid. This is probably due in all cases to the decomposition of a substance called amygdalin under the influence of emulsin or synaptase, a nitrogenized ferment present in the organic structure (see GLUCOSIDES). The reaction is expressed by the equation:



Hydrocyanic acid exists ready formed to a considerable extent in the juice of the bitter cassava.

The presence of hydrocyanic acid is detected with the utmost ease: its remarkable odor and high degree of volatility almost sufficiently characterize it. With solution of silver nitrate it gives a dense curdy white precipitate, much resembling the chloride, but differing from that substance in not blackening so readily by light, in being soluble in boiling nitric acid, and in suffering complete decomposition when heated in the dry state, metallic silver being left: the chloride, under the same circumstances, merely fuses, but undergoes no chemical change. The production of Prussian blue by "Scheele's test" is an excellent and most decisive experiment, which may be made with a very small quantity of the acid. The liquid to be examined is mixed with a few drops of solution of ferrous sulphate and an excess of caustic potash, and the whole exposed to the air for 10 or 15 minutes, with agitation, whereby the ferrous salt is partly converted into ferric salt: hydrochloric acid is then added in excess, which dissolves the precipitated iron oxide, and, if hydrocyanic acid is present, leaves Prussian blue as an insoluble powder. The reaction will be explained in connection with the ferrocyanides (p. 534).

Another very delicate test for hydrocyanic acid will be mentioned in connection with thiocyanic acid.

Metallic Cyanides.—The most important of the metallic cyanides are the following: they bear the most perfect analogy to the haloid salts.

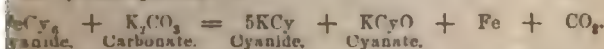
Potassium Cyanide, CNK or KCy.—Potassium heated in cyanogen gas, takes fire and burns in a very beautiful manner, yielding potassium cyanide: the same substance is produced when potassium is heated in the vapor of hydrocyanic acid, hydrogen being liberated. When pure nitrogen is transmitted through a white-hot tube containing a mixture of potassium carbonate and charcoal, a small quantity of potassium cyanide is formed, which settles on the cooler portions of the tube as a white amorphous powder: carbon monoxide is at the same time evolved.* When azotized organic matter of any kind, capable of furnishing ammonia by destructive distillation, as horn-shavings, parings of hides, etc., is heated to redness with potassium carbonate in a close vessel, a very abundant production of potassium cyanide results, which cannot, however, be advantageously extracted by direct means, but in practice is always converted into ferrocyanide, which is a much more stable substance, and crystallizes better.

* According to the experiments of Margueritte and De Sourdeval, the formation of cyanide appears to be more abundant if the potash be replaced by baryta. If the barium cyanide thus formed be exposed to a stream of superheated steam at 500° (i. 572° F.), the nitrogen of the salt is eliminated in the form of ammonia. Margueritte and De Sourdeval recommend this process as a method of preparing ammonia by means of atmospheric nitrogen.

Iron cyanide may be prepared by passing the vapor of hydrocyanic acid into a cold alcoholic solution of potash: the salt is then deposited in crystalline form, and may be separated from the liquid, pressed, and dried. But it is more generally made from the ferrocyanide, which, heated to whiteness in a nearly close vessel, evolves nitrogen and carbon monoxide, and leaves a mixture of carbon, iron carbide, and potassium ferrocyanide, which latter salt is not decomposed unless the temperature is extremely high.

It has given a very easy and excellent process for making potassium cyanide, which does not, however, yield it pure, but mixed with potassium ferrocyanide.

For most of the applications of potassium cyanide, electro-plating, for example, for which a considerable quantity is now used, this impurity is of no consequence. Eight parts of potassium ferrocyanide are rendered anhydrous by gentle heat, and intimately mixed with five parts of dry potassium carbonate: this mixture is thrown into a dry earthen crucible, and kept in fusion, with occasional stirring, until carbon monoxide ceases to be evolved, and the fluid portion of the mass becomes clear. The crucible is left at rest for a moment, and then the clear liquid is decanted from the heavy black sediment at the bottom, which is finely metallic iron in a state of minute division. The reaction is represented by the equation:—



The product may be advantageously used, instead of potassium ferrocyanide, in the preparation of hydrocyanic acid, by distillation with oil of vitriol.

Potassium cyanide is often produced in considerable quantity in blast-furnaces, in which iron ores are smelted with coal or coke.

Potassium cyanide forms colorless, cubic or octohedral, anhydrous crystals, efflorescent in the air, and exceedingly soluble in water: it dissolves in 10 parts of alcohol, but separates in great measure on cooling. It is readily oxidized, and undergoes no change at a moderate red or even white heat, is not deliquescent from air; otherwise, oxygen is absorbed and the cyanide is converted into cyanate. Its solution always has an alkaline reaction, and when exposed to the air exhales the odor of hydrocyanic acid: it is decomposed by the weakest acids, even the carbonic acid of the air, and when boiled in water is slowly converted into potassium formate, with separation of carbon monoxide. It is said to be as poisonous as hydrocyanic acid itself.

Sodium cyanide, NaCy , is a very soluble salt, corresponding closely with potassium cyanide, and obtained by similar means.

Ammonium cyanide, NH_4Cy , is a colorless, crystallizable, and very volatile substance, prepared by distilling a mixture of potassium cyanide and ammonium carbonate; or by mingling the vapor of anhydrous hydrocyanic acid with ammonia gas; or, lastly, by passing ammonia over red-hot charcoal. It is very soluble in water, subject to spontaneous decomposition, and is slightly poisonous.

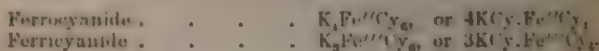
Mercuric cyanide, $\text{Hg}(\text{CN})_2$, or HgCy_2 .—One of the most remarkable properties of cyanogen is its powerful attraction for certain of the less oxidizable metals, and more particularly for mercury and palladium. Dilute hydrocyanic acid dissolves finely-powdered mercuric oxide with the utmost facility, the liquid loses all odor, and yields on evaporation crystals of mercuric cyanide. Potassium cyanide is in like manner decomposed by mercuric cyanide, potassium hydroxide being produced. Mercuric cyanide is generally prepared from potassium ferrocyanide; 2 parts of the salt are dissolved in 10 parts of hot water, and 3 parts of dry mercuric sulphate are added; the mixture is boiled for 15 minutes, and filtered hot from the iron oxide,

which separates. The solution, on cooling, deposits the mercuric cyanide in crystals. Mercuric cyanide forms white, translucent, rhombic prisms, much resembling those of corrosive sublimate: it is soluble in 7 parts of cold water, and in a much smaller quantity at a higher temperature, also in alcohol. The solution has a disagreeable metallic taste, is very poisonous, and is not precipitated by alkalis. Mercuric cyanide is used in the laboratory as a source of cyanogen.

Silver cyanide, AgCy , has been already described (p. 530).—*Zinc cyanide*, ZnCy_2 , is a white insoluble powder, prepared by mixing zinc acetate with hydrocyanic acid.—*Cobalt cyanide*, CoCy_2 , is obtained by similar means: it is dirty-white, and insoluble.—*Palladium cyanide*, PdCy_2 , forms a yellowish-white precipitate when the chloride of that metal is mixed with a solution of cyanide.—*Auric cyanide*, AuCy_3 , is yellowish-white and insoluble, but freely dissolved by solution of potassium cyanide.

Iron Cyanides.—These compounds are scarcely known in the separate state, on account of their great tendency to form double salts. On adding potassium cyanide to a ferrous salt, a yellowish-red flocculent precipitate is formed, consisting chiefly of ferrous cyanide, FeCy_2 , but always containing a certain quantity of potassium cyanide, and dissolved as ferrocyanide by excess of that salt. Ferric cyanide, Fe_3Cy_6 , is known only in solution. Pelouze obtained an insoluble green compound containing Fe_3Cy_6 , or $\text{FeCy}_2 \cdot \text{Fe}_2\text{Cy}_6$, by passing chlorine gas into a boiling solution of potassium ferrocyanide.

The iron cyanides unite with other metallic cyanides, forming two very important groups of compounds, called ferrocyanides and ferricyanides, the composition of which may be illustrated by the respective potassium-salts:—



It will be seen from these formulæ, that ferro- and ferricyanides containing the same quantity of cyanogen, differ from one another only by one atom of univalent metal, and, accordingly, it is found that the former may be converted into the latter, by the action of oxidizing (metal-abstracting) agents, and the latter into the former by the action of reducing (metal-adding) agents. Thus potassium ferrocyanide is easily converted into the ferricyanide by the action of chlorine, and many double ferrocyanides may be formed from ferricyanides by the action of alkalis in presence of a reducing agent: thus potassium ferricyanide, $\text{K}_3\text{Fe}'''\text{Cy}_6$, is easily converted into ammonio-tripotassic ferrocyanide, $(\text{NH}_4)\text{K}_3\text{Fe}''\text{Cy}_6$, by the action of ammonia in presence of glucose.*

Ferrocyanides.

Potassium Ferrocyanide, $\text{K}_4\text{Fe}''\text{Cy}_6$, or $4\text{KCy} \cdot \text{Fe}''\text{Cy}_2$, commonly called *yellow prussiate of potash*.—This important salt is formed—1. By digesting precipitated ferrous cyanide in aqueous solution of potassium cyanide.

* The ferrocyanides and ferricyanides are sometimes regarded as salts of peculiar compound radicals containing iron, viz., *ferrocyanogen*, $\text{Fe}''\text{Cy}_6$, and *ferricyanogen*, $\text{Fe}'''\text{Cy}_3$, the first being quadrivalent, the second trivalent; but this is nothing gained by this assumption. For a discussion of the formulae of these salts and of the double cyanides in general, see Watts's Dictionary of Chemistry, vii. ii. p. 201.

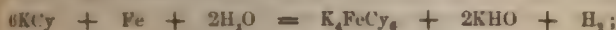
2. By digesting ferrous hydrate with potassium cyanide, potash being formed at the same time :



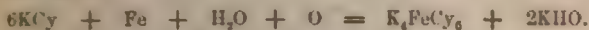
3. Ferrous cyanide with aqueous potash :



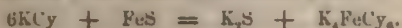
4. Aqueous potassium cyanide with metallic iron : if the air be excluded, hydrogen is evolved :



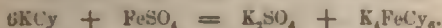
If the air has access to the liquid, oxygen is absorbed, and no hydrogen is evolved :



Ferrous sulphide with aqueous potassium cyanide :

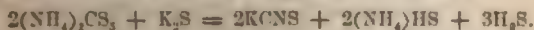


Any soluble ferrous salt with potassium cyanide ; e. g. :

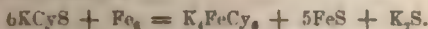


Potassium ferrocyanide is manufactured on the large scale by the following process : Dry refuse animal matter of any kind is fused at a red-heat with impure potassium carbonate and iron filings, in a large iron vessel in which the air should be excluded as much as possible ; potassium cyanide is generated in large quantity. The melted mass is afterwards treated with hot water, which dissolves out the cyanide and other salts, the cyanide being quickly converted by the oxide or sulphide* of iron into ferrocyanide. The filtered solution is evaporated, and the first-formed crystals are purified by re-solution. If a sufficient quantity of iron be not present, great loss is incurred by the decomposition of the cyanide into potassium carbonate and ammonia.

A new process for the preparation of potassium ferrocyanide has lately been proposed by Gélis. It consists in converting carbon bisulphide into ammonium thiocarbonate by agitating it with ammonium sulphide : $\text{CS}_2 + (\text{NH}_4)_2\text{S} = (\text{NH}_4)_2\text{CS}_3$, and heating the product thus obtained with potassium sulphide, whereby potassium thiocyanate (p. 544) is formed, with evolution of ammonium sulphide and hydrogen sulphide :



Potassium thiocyanate is dried, mixed with finely divided metallic iron, and heated for a short time in a closed iron vessel to dull redness, whereby the mixture is converted into potassium ferrocyanide, potassium sulphide, and iron sulphide :



On treatment with water, the sulphide and ferrocyanide of potassium are dissolved, and on evaporation the ferrocyanide is obtained in crystals. It remains to be seen whether this ingenious process is capable of being carried out upon a large scale.

Potassium ferrocyanide forms large, transparent, yellow crystals,

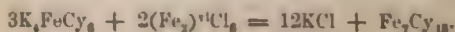
The sulphur is derived from the reduced sulphate of the crude pearl-ashes and animal substances used in the manufacture.

$K_3FeCy_6 + 3Aq.$, derived from an octohedron with a square base: they cleave with facility in a direction parallel to the base of the octohedron, and are tough and difficult to powder. They dissolve in 4 parts of cold and 2 parts of boiling water, and are insoluble in alcohol. They are permanent in the air, and have a mild saline taste. The salt has no poisonous properties, and, in small doses at least, is merely purgative. Exposed to a gentle heat, it loses 3 molecules of water, and becomes anhydrous: at a high temperature it yields potassium cyanide, iron carbide, and various gaseous products; if air be admitted, the cyanide becomes cyanate.

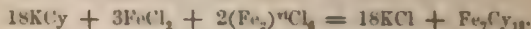
Potassium ferrocyanide is a chemical reagent of great value: when mixed in solution with neutral or slightly acid salts of the heavy metals, it gives rise to precipitates which very frequently present highly characteristic colors. In most of these compounds the potassium is simply displaced by the new metal: the beautiful brown ferrocyanide of copper contains, for example, Cu_2FeCy_6 , or $2CuCy_2 \cdot FeCy_2$, and that of lead, Pb_2FeCy_6 .

With *ferrous salts*, potassium ferrocyanide gives a precipitate which is perfectly white, if the air be excluded and the solution is quite free from ferric salt, but quickly turns blue on exposure to the air. It consists of potassio-ferrous ferrocyanide, $K_3Fe''Cy_6$, or potassium ferrocyanide having half the potassium replaced by iron. The same salt is produced in the preparation of hydrocyanic acid by distilling potassium ferrocyanide with dilute sulphuric acid (p. 529).

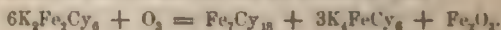
When a soluble ferrocyanide is added to the solution of a *ferric salt*, a deep blue precipitate is formed, consisting of ferric ferrocyanide, Fe_3Cy_{18} , or $Fe'''_3Fe''_2Cy_{18}$, or $2(Fe_2)'''(Cy_6) \cdot FeCy_2$, which in combination with 18 molecules of water constitutes ordinary Prussian blue. This beautiful pigment is best prepared by adding potassium ferrocyanide to ferric nitrate or chloride:



It is also formed by precipitating a mixture of ferrous and ferric salts with potassium cyanide:



This reaction explains Scheele's test for prussic acid (p. 530). Prussian blue is also formed by the action of air, chlorine-water, and other oxidizing agents, on potassio-ferrous ferrocyanide; probably thus:



It is chiefly by this last reaction that Prussian blue is prepared on the large scale, potassium ferrocyanide being first precipitated by ferrous sulphate, and the resulting white or light blue precipitate either left to oxidize by contact with the air, or subjected to the action of nitric acid, chlorine, hypochlorites, chromic acid, etc. The product, however, is not pure ferric ferrocyanide: for it is certain that another and simpler reaction takes place at the same time, by which the potassio-ferrous ferrocyanide (K_3Fe'') $Fe''Cy_6$ is converted, by abstraction of an atom of potassium, into potassio-ferrous ferricyanide (KFe''') $Fe''Cy_6$, which also possesses a fine deep blue color. Commercial Prussian blue is, therefore, generally a mixture of this compound with ferric ferrocyanide, $Fe'''_3Fe''_2Cy_{18}$, the one or the other predominating according to the manner in which the process is conducted.

Prussian blue in the moist state forms a bulky precipitate, which shrinks to a comparatively small compass when well washed and dried by a gentle heat. In the dry state it is hard and brittle, much resembling in appearance the best indigo: the freshly fractured surfaces have a beautiful copper-

red lustre, similar to that produced by rubbing indigo with a hard body. Prussian blue is quite insoluble in water and dilute acids, with the exception of oxalic acid, in a solution of which it dissolves, forming a deep-blue liquid, which is sometimes used as ink: concentrated oil of vitriol converts it into a white, pasty mass, which again becomes blue on addition of water. Alkalies destroy the color instantly: they dissolve out a ferrocyanide, and leave ferric oxide. Boiled with water and mercuric oxide, it yields mercuric cyanide and ferric oxide. Heated in the air, Prussian blue burns like timber, leaving a residue of ferric oxide. Exposed to a high temperature in a close vessel, it gives off water, ammonium cyanide, and ammonium carbonate, and leaves carbide of iron. It forms a very beautiful pigment, both as oil and water color, but has little permanency.

Common or basic Prussian blue is an inferior article, prepared by precipitating a mixture of ferrous sulphate and alum with potassium ferrocyanide, and exposing the precipitate to the air. It contains alumina, which impairs the color, but adds to the weight.

Soluble Prussian blue is obtained by adding ferric chloride to an excess of potassium ferrocyanide; it is insoluble in the saline liquor, but soluble in pure water. It has a deep-blue color, and probably consists of potassium-ferrous ferrocyanide.

Hydrogen Ferrocyanide, Hydroferrocyanic Acid, H_4FeCy_6 , is prepared by decomposing ferrocyanide of lead or copper suspended in water by a stream of sulphuretted hydrogen gas, and separates on evaporating the filtered solution in a vacuum over oil of vitriol. Its solution in water has a powerfully acid taste and reaction, and decomposes alkaline carbonates with effervescence; it does not dissolve mercuric oxide in the cold, but when heat is applied, undergoes decomposition, forming mercuric cyanide and ferrous cyanide: $H_4FeCy_6 + 2HgO = 2HgCy_2 + FeCy_2 + 2H_2O$; but the ferrous cyanide is immediately oxidized by the excess of mercuric oxide, with separation of metallic mercury. In the dry state the acid is very permanent, but when long exposed to the air in contact with water, it is entirely converted into Prussian blue.

Sodium Ferrocyanide, $Na_4FeCy_6 \cdot 12Aq.$, crystallizes in yellow four-sided prisms, which are efflorescent in the air, and very soluble.

Ammonium Ferrocyanide, $(NH_4)_4FeCy_6 \cdot 3Aq.$, is isomorphous with potassium ferrocyanide: it is easily soluble, and is decomposed by ebullition. **Barium Ferrocyanide, Ba_2FeCy_6 ,** prepared by boiling potassium ferrocyanide with a large excess of barium chloride, or Prussian blue with baryta-water, forms minute yellow, anhydrous crystals, which have but a small degree of solubility even in boiling water. The corresponding compounds of *strontium*, *calcium*, and *magnesium* are more freely soluble. The ferrocyanides of *silver*, *lead*, *zinc*, *manganese*, and *bismuth* are white and insoluble; those of *nickel* and *cobalt* are pale-green and insoluble; and lastly, that of *copper* has a beautiful reddish-brown tint.

There are also several double ferrocyanides. When, for example, concentrated solutions of calcium chloride and potassium ferrocyanide are mixed, sparingly soluble crystalline precipitate falls, containing $K_2CaFeCy_6$.

Ferricyanides.

These salts are formed, as already observed, by abstraction of metal from the ferrocyanides, in other words, by the action of oxidizing agents.

Potassium Ferricyanide, $K_3Fe^{III}Cy_6$, or $K_3(Fe^{III})Cy_6$, often called *red prussiate of potash*, is prepared by slowly passing chlorine, with agita-

tion, into a somewhat dilute and cold solution of potassium ferriyanide, until the liquid acquires a deep reddish-green color, and ceases to precipitate a ferric salt. The solution is evaporated until a skin is given, then upon the surface, then filtered and left to cool, and the salt is purified by re-crystallization. It forms prismatic, or sometimes tabular crystals, belonging to the monoclinic system, of a beautiful ruby-red tint, permanent in the air, and soluble in 4 parts of cold water: the solution has a dark-greenish color. The crystals burn and emit sparks when introduced into the flame of a candle. The salt is decomposed by excess of chlorine, and by deoxidizing agents, as sulphuretted hydrogen.

Hydrogen ferriyanide is obtained in the form of a reddish-brown solid liquid, by decomposing lead ferriyanide with sulphuric acid: it is very unstable, and is resolved by boiling into hydrated ferric cyanide, an insoluble dark-green powder containing $\text{Fe}_2\text{Cy}_4 \cdot 3\text{Aq.}$, and hydrocyanic acid. The ferriyanides of *ashum*, *ammonium*, and of the *alkaline earths*, *oxides*, are soluble: those of most of the other metals are insoluble. Potassium ferriyanide added to a ferric salt occasions no precipitate, but merely a darkening of the reddish-brown color of the solution; with *ferrous salts*, on the other hand, it gives a deep-blue precipitate, consisting of ferrous ferri-cyanide, $\text{Fe}_2\text{Cy}_{17} + x\text{Aq.}$, or $\text{Fe}^{++}(\text{Fe}^{+++}\text{Cy}_6)_x + x\text{Aq.}$, which, when dry, has a brighter tint than Prussian blue: it is known under the name of *Perrin's blue*. Hence, potassium ferriyanide is as delicate a test for ferrous salts as the yellow ferriyanide is for ferric salts.

CORALICYANIDES.—This name is applied to a series of compounds analogous to the preceding, containing cobalt in place of iron: a hydrogen-acid has been obtained, and a number of salts, which much resemble the ferri-cyanides. Several other metals of the same isomorphous family are found capable of replacing iron in these compounds.

NITROPRUSSIDES.—These are salts produced by the action of nitric acid upon ferri-cyanides and ferriyanides. The general formula of these salts appears to be $\text{M}_2(\text{NO})\text{Fe}^{+++}\text{Cy}_6$, which exhibits a close relation to those of the ferri- and ferriyanides.

The formation of the nitroprussides appears to consist in the reduction of the nitric acid to the state of nitrogen dioxide or nitrosyl, NO , which replaces 1 molecule of metallic cyanide, M^+Cy , in a molecule of ferriyanide $\text{M}_2\text{Fe}^{+++}\text{Cy}_6$. The formation of these salts is attended with the production of a variety of secondary products, such as cyanogen, oxamide, hydrocyanic acid, nitrogen, carbonic acid, &c. One of the finest compounds of this series is the nitroprusside of sodium, $\text{Na}_2(\text{NO})\text{Fe}^{+++}\text{Cy}_6 + 2\text{Aq.}$, which is readily obtained by treating 2 parts of powdered potassium ferriyanide with 5 parts of common nitric acid previously diluted with its own volume of water. The solution, after the evolution of gas has ceased, is digested on the water-bath, until ferrous salts no longer yield a blue, but a blue-colored precipitate. The liquid is now allowed to cool, when much potassium nitrate, and occasionally oxamide, is deposited: it is filtered and neutralized with sodium carbonate, which yields a green or brown precipitate, and a ruby-colored filtrate. This, on evaporation, gives a crystallization of the nitrates of potassium and sodium, together with the nitroprusside. The crystals of the latter are selected and purified by crystallization: they are rhombic and of a splendid ruby color. The soluble nitroprussides strike a most beautiful violet tint with soluble sulphides, affording an extremely delicate test for alkaline sulphides.

ALCOHOLIC CYANIDES OR HYDROCYANIC ETHERS.

These compounds play an important part in organic chemistry: for example, in the conversion of alcohols into acids containing a greater number of carbon-atoms.

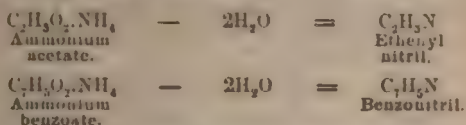
The cyanides of univalent alcohol-radicles may also be regarded as compounds of nitrogen with trivalent radicles: hence, as already observed (p. 527), they are often called nitrils.

These alcoholic cyanides are produced:—

1. By distilling a mixture of potassium-cyanide and the potassium-salt of ethylsulphuric acid, $\text{C}_2\text{H}_5 \left\{ \begin{array}{l} \text{H} \\ \text{SO}_4 \end{array} \right.$, or a similar acid:—

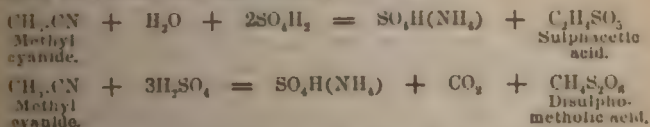


2. By the dehydrating action of phosphoric oxide on the ammonium-salts of the monobasic acids, $\text{C}_2\text{H}_5\text{O}_2\text{NH}_4$ and $\text{C}_6\text{H}_5\text{O}_2\text{NH}_4$, homologous with acetic and benzoic acid respectively, thus:—

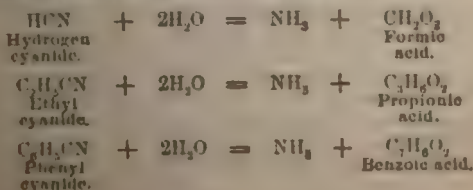


The bodies obtained by these two processes are oily liquids, exhibiting the same properties whether prepared by the first or the second method, excepting that those obtained by the latter have an aromatic fragrant odor, whereas those prepared by the former have a pungent and repulsive odor, due to the presence of certain isomeric compounds, to be noticed further on. *Methyl cyanide*, *Ethetyl-nitril*, or *Acetonitril*, boils at 77°C . (170.6°F .); *Ethyl cyanide*, or *Propylnitril*, at 82°C . (179.6°F .); *Butyl cyanide*, or *Valeronitril*, at $125\text{--}128^\circ \text{C}$. ($257\text{--}262.4^\circ \text{F}$.); *Isopentyl cyanide*, *Amyl cyanide*, or *Capronitril*, at 146°C . (294.8°F .); *Phenyl cyanide*, or *Benzonitril*, at 190.6°C . (375°F .).

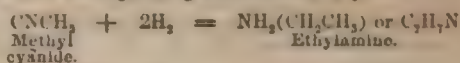
All these cyanides, when heated with fuming sulphuric acid or sulphuric oxide, are converted into sulpho-acids; thus:—



By heating with caustic potash or soda, they are resolved into ammonia and the corresponding fatty or aromatic acid, just as hydrocyanic acid similarly treated is resolved into ammonia and formic acid; thus:—



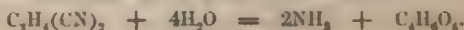
The alcoholic cyanides or nitrils, treated with nascent hydrogen, are converted into the corresponding amine-bases, *e. g.* :—



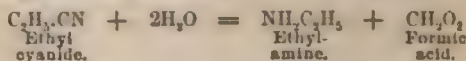
Ethene Cyanide, $(\text{C}_2\text{H}_4)_n(\text{CN})_n$, is obtained by distilling potassium cyanide with ethene iodide :—



It is a crystalline body, melting at 50°C . (140°F .), and converted by alcoholic potash into ammonia and succinic acid :—

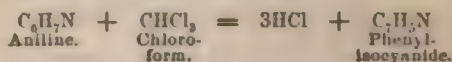


Isocyanides, or Carbamines.—On examining the equations just given for the decomposition of the alcoholic cyanides under the influence of alkalis, it is easy to see that the reaction might be supposed to take place in a different way, each cyanide yielding, not ammonia and an acid containing the same number of carbon-atoms as itself, but an alcoholic ammonia or amine, and formic acid ; thus :—



In the one case the alcohol-radicle remains united with the carbon, producing a homologue of formic acid, together with ammonia ; in the other it remains united with the nitrogen, producing a homologue of ammonia, together with formic acid.

A class of cyanides exhibiting the second of these reactions has been discovered by Dr. Hofmann.* They are obtained by distilling a mixture of an alcoholic ammonia-base and chloroform with alcoholic potash : for example :—



The potash serves to neutralize the hydrochloric acid produced, which would otherwise quickly decompose the isocyanide. Phenyl-isocyanide, or phenyl-carbamine, when freed from excess of aniline by oxalic acid, then dried with caustic potash and rectified, is an oily liquid, green by transmitted, blue by reflected light, and having an intolerably pungent and suffocating odor. It is isomeric with benzonitril, and is resolved by boiling with dilute acids into formic acid and aniline :—



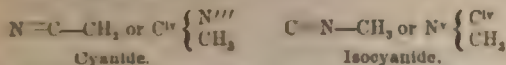
It is a remarkable fact that, whereas the normal alcoholic cyanides are easily decomposed by boiling alkaline solutions, the isocyanides are scarcely altered by alkalis, but are easily hydrated under the influence of acids.

The isocyanides of ethyl and amyl have been obtained by similar processes ; namely, by distilling methylamine and ethylamine respectively with chloroform, also by the action of ethylic and amylic iodides on silver cyanide. They resemble the phenyl compound in their reactions, and are also characterized by extremely powerful odors. The repulsive odor possessed by the normal alcoholic cyanides when prepared by distilling potash-

* Proceedings of the Royal Society, xvi. 144, 145, 150.

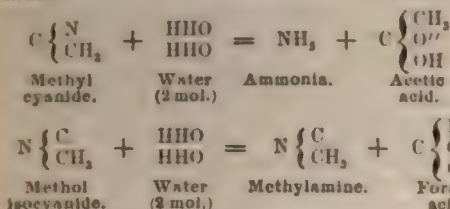
in cyanide with the ethyl-sulphates or homologous salts, appears to be due to the presence of small quantities of these isocyanides.

The difference of constitution between the normal cyanides and the isocyanides may be represented by the following formulæ, taking the methyl compounds for example :—



In the isocyanide the carbon belonging to the alcohol-radicle is united directly with the nitrogen; in the cyanide, only through the medium of the nitrogen belonging to the cyanogen.

This difference of structure may perhaps account for the difference in actions of the cyanides and isocyanides, under the influence of hydrating agents, thus :



The isocyanides of methyl and ethyl (methyl- and ethyl-carbamines) unite with acids, forming crystallizable salts.

OXYGEN- AND SULPHUR-COMPOUNDS OF CYANOGEN.

Cyanic Acid, CHNO .—Of this acid there are two possible modifications represented by the formulæ :



These modifications are actually exhibited in the metallic cyanates and cyanic ethers; but the acid itself is known in one modification only, the particular constitution of which has not yet been determined. It is obtained when cyanuric acid, deprived of its water of crystallization, is heated to dull redness in a hard glass retort connected with a receiver cooled by ice. The cyanuric acid is resolved, without any other product, into cyanic acid, which condenses in the receiver to a limpid, colorless liquid, of exceedingly pungent and penetrating odor, like that of the strongest acetic acid: it even blisters the skin. When mixed with water it decomposes almost immediately, giving rise to ammonium bicarbonate :

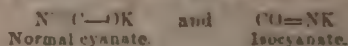


In consequence of this decomposition, cyanic acid cannot be separated from a cyanate by a stronger acid. A trace of it, however, always escapes decomposition, and communicates to the carbon dioxide evolved a pungent smell similar to that of sulphurous acid. The cyanates may be easily distinguished by this smell, and by the simultaneous formation of an ammonium-salt, which remains behind.

Pure cyanic acid cannot be preserved: shortly after its preparation it

changes spontaneously, with sudden rise of temperature, into a solid white, opaque, amorphous substance, called *cyanide*. This body has the same composition as cyanic acid: it is insoluble in water, alcohol, ether, and dilute acids: it dissolves in strong oil of vitriol by the aid of heat with evolution of carbon dioxide and production of ammonia; heated with a solution of caustic alkali, it dissolves, ammonia being disengaged, and a mixture of cyanate and cyanurate of the base generated. By dry distillation it is reconverted into cyanic acid.

Potassium Cyanate, CNKO .—Of this salt there are two modifications, viz.



The normal cyanate, formed by passing gaseous cyanogen chloride (p. 544) into cold aqueous potash, crystallizes in long needles, and is converted by fusion into the isocyanate.

The isocyanate (ordinary potassium cyanate) is best prepared by oxidizing potassium cyanide with litharge. The cyanide, already containing a portion of cyanate, described at page 531, is remelted in an earthen crucible, and finely powdered lead oxide added by small portions; the oxide is instantaneously reduced, and the metal, at first in a state of minute division, ultimately collects to a fused globule at the bottom of the crucible. The salt is poured out, and, when cold, powdered and boiled with alcohol; the hot filtered solution deposits crystals of potassium isocyanate on cooling. The great deoxidizing power exerted by potassium cyanate at a high temperature renders it a valuable agent in many of the finer metallurgical operations.

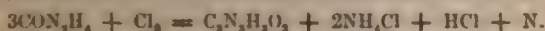
Another method of preparing the isocyanate is to mix dried and finely powdered potassium ferrocyanide with half its weight of equally dry manganese dioxide; heat this mixture in a shallow non-ladle, with free exposure to air and frequent stirring, until the tinder-like combustion is at an end; and boil the residue in alcohol, which extracts the isocyanate.

The salt crystallizes from alcohol in thin, colorless, transparent plates, which suffer no change in dry air, but on exposure to moisture are gradually converted, without much alteration of appearance, into potassium bicarbonate, ammonia being at the same time given off. Water dissolves potassium isocyanate in large quantity; the solution is slowly decomposed in the cold, and rapidly at a boiling heat, into potassium bicarbonate and ammonia. When a concentrated solution is mixed with a small quantity of dilute mineral acid, a precipitate falls, consisting of acid potassium cyanurate. Potassium isocyanate is reduced to cyanide by ignition with charcoal in a covered crucible. Mixed with solutions of lead and silver, it gives rise to white insoluble isocyanates of those metals.

Ammonium Cyanate (probably *iso*), $\text{CN}, \text{H}_4\text{O}$, or NH_4CNO .—When the vapor of cyanic acid is mixed with excess of ammoniacal gas, a white, crystalline, solid substance is produced, which has all the characters of a true, although not neutral ammonium cyanate. It dissolves in water, and if mixed with an acid, evolves carbon dioxide; with an alkali, it yields ammonia. But if the solution be heated, or if the crystals be merely exposed for a certain time to the air, a portion of ammonia is dissipated, and the properties of the compound are completely changed. It may now be mixed with acids without the least sign of decomposition, and does not evolve the smallest trace of ammonia when treated with cold caustic alkali. The result of this transformation, as already observed (p. 469), is a true

Cyanuric Acid, $\text{C}_3\text{N}_3\text{H}_3\text{O}_3$.—This substance may be prepared by heating dry and pure urea in a flask or retort; the urea melts, loses off ammonia in large quantity, and at length becomes converted into a

grey-white, solid, amorphous mass, which is impure cyanuric acid. This dissolved by the aid of heat in strong oil of vitriol, and nitric acid added in small portions till the liquid becomes nearly colorless; it is then mixed with water, and left to cool, whereupon the cyanuric acid separates. The acid may likewise be decomposed very conveniently by gently heating it in a tube, while dry chlorine or hydrochloric acid gas passes over it. A mixture of cyanuric acid and sal-ammoniac results, which is separated by boiling the latter in water. The reaction with chlorine is represented by the equation:



Cyanuric acid forms colorless efflorescent crystals, seldom of large size, derived from an oblique rhombic prism. It is very little soluble in cold water, and requires 24 parts for solution at a boiling heat: it reddens litmus slightly, has no odor, and but little taste. The acid is tribasic: the crystals contain $\text{C}_3\text{N}_3\text{H}_3\text{O}_3 \cdot 2\text{Aq}$, and are easily deprived of their water of crystallization. In point of stability, cyanuric acid offers a most remarkable contrast to its isomeride, cyanic acid; it dissolves, as above indicated, in oil of vitriol, and even in strong nitric acid, without decomposition, but, in fact, crystallizes from the latter in the anhydrous state. Long-continued boiling with these powerful agents resolves it into ammonia and carbonic acid.

The connection between cyanic acid, urea, and cyanuric acid, may be recapitulated:

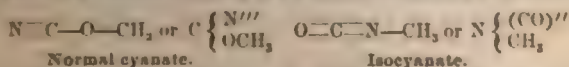
Ammonium cyanate is converted by heat into urea.

Urea is decomposed by the same means into cyanuric acid and ammonia.

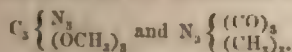
Cyanuric acid is changed by a very high temperature into cyanic acid, one molecule of cyanuric acid splitting into three molecules of cyanic acid.

Cyanic and Cyanuric Ethers.

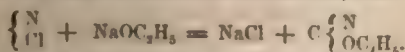
Of each of these ethers there are two series, analogous to the alcoholic cyanates and isocyanides. The difference of their structure is exhibited by the following formulæ, taking the methyl-compounds as examples:



The corresponding cyanuric ethers are represented by the formulæ,



The normal cyanic ethers, discovered by Cloez, and the normal cyanuric ethers, discovered by Hofmann,* are produced simultaneously by the action of gaseous cyanogen chloride on the sodium alcohols: normal ethyl cyanate, for example, from cyanogen chloride and sodium ethylate; thus:



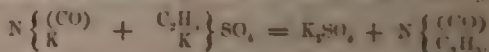
* The isocyanic and isocyanuric ethers having been discovered first (by Wurtz & 1840), were originally called cyanic and cyanuric ethers.

They are decomposed by water, assisted by acids or bases, into cyanic or cyanuric acid and an alcohol: *e. g.*:



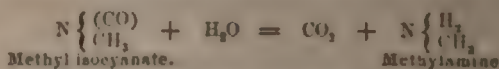
The cyanates of methyl, ethyl, and amyl are colorless, oily liquids, decomposed by heat into a volatile portion and a solid residue. The corresponding cyanurates are crystalline solids.

The isocyanic and isocyanuric ethers, or alcoholic carbamides, are produced simultaneously by distilling a dry mixture of potassium isocyanate and methylsulphate, ethylsulphate, etc., *e. g.*:



Ethyl isocyanate and isocyanurate thus obtained are easily separated by distillation, the former boiling at 60° C. (140° F.), the latter at 27° C. (528.80° F.). The former is a mobile liquid, the latter a crystalline solid melting at 85° C. (185° F.). The isocyanurate may likewise be obtained by distilling a mixture of potassium cyanurate and ethylsulphate.

The ethers of this class, when heated with a strong solution of caustic alkali, are resolved into carbon dioxide and an alcoholic ammonia or amine. *e. g.*:



Fulminic Acid, $C_2N_2H_2O_2$.—This compound, polymeric with cyanic and cyanuric acids, is one of the products formed by the action of nitrous acid upon alcohol in presence of a salt of silver or mercury. The acid itself, or hydrogen fulminate, has not been obtained.

Silver fulminate is prepared by dissolving 40 or 50 grains of silver, which need not be pure, in about $\frac{3}{4}$ oz. by measure of nitric acid of sp. gr. 1.47, with the aid of a little heat. To the highly acid solution, while still hot, 2 measured ounces of alcohol are added, and heat is applied until reaction commences. The nitric acid oxidizes part of the alcohol to aldehyde and oxalic acid, becoming itself reduced to nitrous acid, which, in turn, acts upon the alcohol in such a manner as to form nitrous ether, fulminic acid, and water, 1 molecule of nitrous ether and 1 molecule of nitrous acid containing the elements of 1 molecule of fulminic acid and 2 molecules of water:



The silver fulminate slowly separates from the hot liquid, in the form of small, brilliant, white, crystalline plates, which may be washed with a little cold water, distributed upon separate pieces of filter-paper in portions not exceeding a grain or two each, and left to dry in a warm place. When dry, the papers are folded up and preserved in a box. The only perfectly safe method of keeping the salt is by immersing it in water. Silver fulminate is soluble in 36 parts of boiling water, but the greater part crystallizes out on cooling. It is one of the most dangerous substances known, exploding with forced violence when strongly heated, or when rubbed or struck with a hard body, or when touched with concentrated sulphuric acid; the metal is consumed, and a large volume of gaseous matter suddenly evolved. Nevertheless, when very cautiously mixed with sugar-candy it may be turned to a cube with as much facility as any other organic

stance. Its composition thus determined is expressed by the formula $C_2N_4O_4$.

Fulminic acid is bibasic: when silver fulminate is digested with caustic alkali, one-half of the silver is precipitated as oxide, and a *silver-potassium fulmate*, $AgKC_2N_4O_4$, is produced, which resembles the neutral silver-salt, and detonates by a blow. Corresponding compounds containing sodium or ammonium exist: but a pure fulminate of an alkali-metal has never been obtained. If silver fulminate be digested with water and copper, or zinc, silver is entirely displaced, and a fulminate of the other metal produced. The zinc-salt mixed with baryta-water gives rise to a precipitate of zinc oxide, while *zincobaric fulminate*, $ZnBa(C_2N_4O_4)_2$, remains in solution.

Mercuric fulminate, $HgC_2N_4O_4$, is prepared by a process very similar to that by which the silver-salt is obtained. One part of mercury is dissolved in 12 parts of nitric acid; the solution is mixed with an equal quantity of alcohol; and gentle heat is applied, the reaction, if too violent, moderated by adding more spirit from time to time. Much carbonic dioxide, nitrogen, and red vapors are disengaged, together with a large quantity of nitrous ether and aldehyde; these are sometimes condensed and rectified for sale, but are said to contain hydrocyanic acid. The mercuric fulmate separates from the hot liquid, and after cooling may be purified by admixture of reduced metal by solution in boiling water and re-precipitation. It much resembles the silver-salt in appearance, proper-ty, and degree of solubility. It explodes violently by friction or percussion, but unlike the silver-compound, merely burns with a sudden and not noiseless flash when kindled in the open air. It is manufactured on a large scale for the purpose of charging *percussion-caps*; sulphur and potassium chlorate, or more frequently nitre, are added, and the powder, pressed into the cap, is secured by a drop of varnish.

The relation of composition between the three isomeric acids is shown by a comparison of their silver-salts: the first acid is monobasic, the second dibasic, and the third tribasic:—

| | | | | | | |
|------------------|---|---|---|---|---|-----------------|
| Silver cyanate | . | . | . | . | . | $AgCNO$ |
| Silver fulminate | . | . | . | . | . | $Ag_2C_2N_4O_4$ |
| Silver cyanurate | . | . | . | . | . | $Ag_3C_3N_3O_3$ |

Fulminic, as well as cyanic acid, may be converted into urea. Dr. Berzelius has shown that, when a solution of copper fulminate is mixed with an excess of ammonia, filtered, treated with sulphuretted hydrogen in excess, and again filtered from the insoluble copper sulphide, the liquid filtered is a mixed solution of urea and ammonium thiocyanate.

Another view regarding the constitution of fulminic acid was proposed by Gerhard. The fulminates may be considered as methyl cyanide (acetonitril), in which one atom of hydrogen is replaced by NO_2 , and 2 atoms of hydrogen by mercury or silver:—

| | | | | | | |
|------------------|---|---|---|---|---|---------------------|
| $C\ H\ H\ H\ CN$ | . | . | . | . | . | Methyl cyanide. |
| $C(NO_2)AgAgCN$ | . | . | . | . | . | Silver fulminate. |
| $C(NO_2)Hg''CN$ | . | . | . | . | . | Mercuric fulminate. |

This view has received some support by the interesting observation, made by Kekulé, that the action of chlorine upon mercuric fulminate, leads to the formation of chloropierin, $C(NO_2)Cl$, (p. 526). The constitution of fulminic acid with the methyl series is thus established.

Fulminuric Acid, $C_2N_4H_2O_4$.—This acid, isomeric with cyanuric acid, was discovered simultaneously by Liebig and by Schischkoff. It is obtained by the action of a soluble chloride upon mercuric fulminate. On

boiling mercuric fulminate with an aqueous solution of potassium chloride, the mercury salt gradually dissolves, and the clear solution, after some time, becomes turbid, in consequence of a separation of mercuric oxide; it then contains potassium fulminate:—



If, instead of potassium chloride, sodium or ammonium chloride be employed, the corresponding sodium and ammonium-compounds are obtained. The fulminates crystallize with great facility: they are not explosive.

Fulminuric acid has the same composition as cyanuric acid, but it is bibasic, whereas cyanuric acid is tribasic.

Cyanogen Chlorides.—Chlorine forms with cyanogen, or its elements, two compounds, which are polymeric, and analogous to cyanic and cyanuric acids. *Gaseous cyanogen chloride*, CyCl , is formed by passing chlorine gas into anhydrous hydrocyanic acid, or by passing chlorine over moist mercuric cyanide contained in a tube sheltered from the light. It is a permanent and colorless gas at the temperature of the air, of insupportable pungency, and soluble to a very considerable extent in water, alcohol, and ether. At -18°C . (0.4°F .) it congeals to a mass of colorless crystals, which at -15°C . (5°F .) melt to a liquid whose boiling point is -11.6°C . (12.3°F .). At the temperature of the air it is condensed to the liquid form under a pressure of four atmospheres, and when long preserved in this state in hermetically sealed tubes, gradually passes into the solid modification.

On passing gaseous cyanogen chloride into a solution of ammonia in anhydrous ether, cyanamide, CN_2H_2 , is formed together with ammoniac.

Solid cyanogen chloride, $\text{C}_3\text{N}_3\text{Cl}_3$, or Cy_3Cl_3 , is generated when anhydrous hydrocyanic acid is put into a vessel of chlorine gas, and the whole exposed to the sun: hydrochloric acid is formed at the same time. It forms long colorless needles, which exhale a powerful and offensive odor, compared by some to that of the excrement of mice; it melts at 140°C . (284°F .), and sublimes unchanged at a higher temperature. When heated in contact with water, it is decomposed into cyanuric and hydrochloric acid. It dissolves in alcohol and ether without decomposition.

Cyanogen Bromide and Iodide correspond with the first of the preceding compounds, and are prepared by distilling bromine or iodine with mercuric cyanide. They are colorless, volatile, solid substances, of powerful odor.

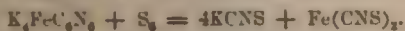
Cyanogen Sulphide, $\text{C}_2\text{N}_2\text{S}$, or Cy_2S , recently obtained by Linnemann by the action of cyanogen iodide upon silver thiocyanate, crystallizes in transparent, volatile, rhombic plates, having an odor similar to that of cyanogen iodide. It melts at 60°C . (140°F .), but decomposes rapidly at a higher temperature; dissolves in ether, alcohol, and water, and separates from hot concentrated solutions, on cooling, in the crystalline form.

Thiocyanic Acid, CNHS , also called *Sulphocyanic acid*.—This acid is the sulphur analogue of cyanic acid, and, like the latter, is monobasic, the thiocyanates of monad metals being represented by the formula MCNS .

Potassium Thiocyanate, CNKS .—To prepare this salt, yellow potassium ferrocyanide, deprived of its water of crystallization, is intimately mixed with half its weight of sulphur, and the whole heated to tranquil fusion in an iron pot, and kept for some time in that condition. When cold, the melted mass is boiled with water, which dissolves out a mixture of potassium thiocyanate and iron thiocyanate, leaving little behind but the excess

sulphur. This solution, which becomes red on exposure to the air, is mixed with potassium carbonate, by which iron is precipitated, and potassium substituted: an excess of the carbonate must be, as far as possible, avoided. The filtered liquid is concentrated, by evaporation over an open fire, to a small bulk, and left to cool and crystallize. The crystals are drained, purified by re-solution, if necessary, or dried by inclosing them, spread on filter-paper, over a surface of vitriol covered with a bell-jar.

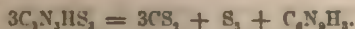
The reaction between the sulphur and the potassium ferrocyanide is represented by the equation:—



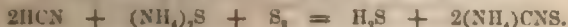
Another, and even better process, consists in gradually heating to low heat in a covered vessel a mixture of 46 parts of dried potassium ferrocyanide, 32 of sulphur, and 17 of pure potassium carbonate. The mass exhausted with water, the aqueous solution is evaporated to dryness, the residue is exhausted with alcohol. The alcoholic liquid deposits solid crystals on cooling or evaporation.

Potassium thiocyanate crystallizes in long, slender, colorless prisms, or plates, which are anhydrous: it has a bitter saline taste, and is destitute of poisonous properties: it is very soluble in water and alcohol, and deliquesces when exposed to a moist atmosphere. When heated, it melts to a colorless liquid, at a temperature far below that of ignition.

When passed into a strong solution of potassium thiocyanate, throws down a large quantity of a bulky, deep-yellow, insoluble substance, formerly called sulphocyanogen, from its supposed identity with the isocyanates of the sulphocyanates: it is, however, invariably found to contain iron, and is represented by the formula $C_2N_2HS_2$. This yellow substance, now generally called persulphocyanogen, is quite insoluble in water, alcohol, and ether. When heated in the dry state, it evolves sulphur and carbon bisulphide, and leaves a pale, straw-yellow substance called hydromellone, $C_2N_2H_2$, the decomposition being represented by the equation:—



Hydrogen Thiocyanate, or *Thiocyanic Acid*, $HCNS$, is obtained by decomposing lead thiocyanate, suspended in water, with sulphuretted hydrogen. The filtered solution is colorless, very acid, and not poisonous: it is easily decomposed, in a very complex manner, by ebullition, and by exposure to air. By neutralizing the liquid with ammonia, and evaporating very slowly to dryness, ammonium thiocyanate, NH_4CNS , is obtained as a deliquescent, saline mass. The salt may be conveniently prepared by digesting hydrocyanic acid with yellow ammonium sulphide (containing excess of sulphur), and boiling off the excess of the latter:—



Thiocyanates of sodium, barium, strontium, calcium, manganese, and ferrous cyanate, are colorless and very soluble; those of lead and silver are insoluble. A soluble thiocyanate mixed with a ferric salt gives a precipitate, but causes the liquid to assume a blood-red tint: hence the use of potassium thiocyanate as a test for iron in the state of ferric salt. The red color produced by thiocyanates in ferric solutions is exactly like that caused under similar circumstances by meconic acid. The two substances may, however, be readily distinguished by the addition of a solution of gold chloride, which destroys the color produced by thiocyanates. Ferric meconate may also be distinguished from the thiocyanate by an

mate, $N(CS)''(C_6H_5)_2$, in like manner from dinaphthylsulphocarbamide. The former boils at $220^\circ C.$ ($428^\circ F.$).

Allyl Isothiocyanate, or **Allylic Thiocarbimide**, $N \left\{ \begin{smallmatrix} (CS)'' \\ C_3H_5 \end{smallmatrix} \right.$.—This is the intensely pungent volatile oil obtained by distilling the seeds of black mustard with water. It does not exist ready-formed in the seeds, but is produced by the decomposition of myronic acid under the influence of rosolin, an albuminous substance analogous to the synaptase of bitter almonds. The same compound, or perhaps its isomeride, normal allyl cyanate, is produced by the action of potassium thiocyanate or silver cyanate on allyl iodide or allyl oxide.

Oil of mustard is a transparent, colorless, strongly refracting oil, possessing in the highest degree the sharp penetrating odor of black mustard. The smallest quantity of the vapor excites tears, and is apt to produce inflammation of the eyes. It has a burning taste, and rapidly blisters the skin. Its specific gravity is 1.009 at $15^\circ C.$ ($59^\circ F.$). It boils at $148^\circ C.$ ($300^\circ F.$). It is sparingly soluble in water, easily soluble in alcohol and ether; dissolves sulphur and phosphorus when heated, and deposits them in the crystalline state on cooling. It is violently oxidized by nitric and chromic acids. Heated in a sealed tube with potassium monosulphide, it yields potassium thiocyanate and allyl sulphide (volatile oil of garlic).



It likewise yields garlic oil when decomposed by potassium. Heated to $200^\circ C.$ ($392^\circ F.$) in a sealed tube with pulverized soda-lime, it yields sodium thiocyanate and allyl oxide, the oxidized constituent of garlic oil:



Aqueous potash, soda, baryta, and the oxides of lead, silver, and mercury, in the presence of water, convert oil of mustard into sinapoline, $C_7H_{12}N_2O$, with the formation of metallic sulphide and carbonate; thus:



Sinapoline is a basic substance, which crystallizes in colorless plates, soluble in water and alcohol, and having a distinct alkaline reaction.

Oil of mustard readily unites with ammonia, forming thiosinamine,

$(C_3H_5)NS.NH_3$, or allyl-thiocarbamide, $N_2 \left\{ \begin{smallmatrix} (CS)'' \\ C_3H_5 \\ H_3 \end{smallmatrix} \right.$, which is also a

volatile compound, forming colorless prismatic crystals, having a bitter taste, soluble in water. The solution does not affect test-paper. Thiosinamine melts when heated, but cannot be sublimed. Acids combine with it, but do not form crystallizable salts; the double salts of the hydrochloride with platinum and mercuric chlorides are the most definite.

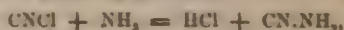
Thiosinamine is decomposed by metallic oxides, as lead oxide or mercuric oxide, with production of a metallic sulphide and sinamine, $C_4H_6N_2$, a volatile compound which crystallizes very slowly from a concentrated aqueous solution, in brilliant, colorless crystals containing water. It has a powerfully bitter taste, is strongly alkaline to test-paper, and decomposes ammonium salts at the boiling heat. Its oxalate is crystallizable. The formation of sinamine from thiosinamine by the action of mercuric oxide is represented by the equation, $C_3H_5N_2S + HgO = HgS + H_2O + C_4H_6N_2$.

Seleniocyanates.—A series of salts containing selenium, and corresponding in composition and properties with the thiocyanates, have been discovered and examined by Mr. Crookes.*

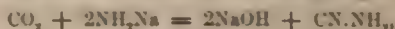
* *Journal of the Chemical Society*, iv. 12.

AMIDO-DERIVATIVES OF CYANIC AND CYANTRIC ACIDS.

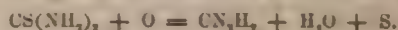
Cyanamide, CN.NH_2 , is formed by the action of chloride or bromide of cyanogen on ammonia dissolved in ether:



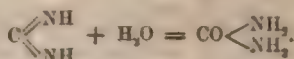
also by the action of carbon dioxide on sodamide, NH_2Na :



and by desulphurizing thiocarbamide with oxide of lead or mercury:

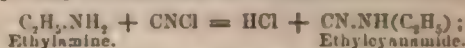


Cyanamide forms colorless crystals, easily soluble in water, alcohol, and ether, melting at 40°C . (104°F .). The solutions give with ammoniacal silver nitrate a yellow precipitate of argentocyanamide, CN_2Ag , and with cupric sulphate a black precipitate of cuprocyanamide, CN_4Cu . By nitric, sulphuric, or phosphoric acid cyanamide is converted into carbamide, $\text{CO}(\text{NH}_2)_2$. In this and most of its reactions it behaves as if it had the structure of carbodiimide, $\text{C} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}$; thus:

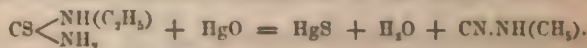


Hydrogen sulphide converts it, in like manner, into thiocarbamide, $\text{CS}(\text{NH}_2)_2$.

Alcoholic derivatives of cyanamide are formed by the action of cyanogen chloride on primary amines dissolved in ether:



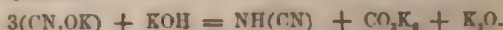
also by heating the corresponding thiocarbamides with mercuric oxide and water:



Methyl-cyanamide and *Ethyl-cyanamide* are thick uncrystallizable syrups, having a neutral reaction, and easily converted into polymeric modifications.

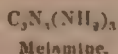
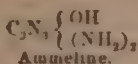
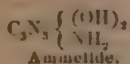
Allyl-cyanamide, $\text{CN.NH}(\text{C}_3\text{H}_5)$, prepared from allyl-thiocarbamide, easily changes into the polymeric compound, triallyl melamine, $\text{C}_6\text{H}_9\text{N}_3$, $(\text{C}_3\text{H}_5)_3$.

Dicyanamide, $\text{NH}(\text{CN})_2$, is formed by the action of potash on normal potassium cyanate:



Dicyanodiamide, $\text{C}_2\text{N}_4\text{H}_4 = \text{C}_2\text{N}_4(\text{NH})_2$ (*Diam*), is formed, by polymerization of cyanamide, when the aqueous solution of the latter is left to itself, or evaporated; also when thiocarbamide is boiled with mercuric oxide or silver oxide. It is easily soluble in water and in alcohol, and crystallizes in rhombic plates, melting at 205°C . (401°F .). On adding silver nitrate to its aqueous solution, the compound $\text{C}_2\text{N}_4\text{H}_4\text{Ag} + \text{NO}_2\text{H}$ crystallizes out in silky needles.

Cyanuramides.—From cyanuric acid, $C_3N_3(OH)_3$, may be derived three amides, viz.:



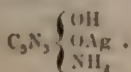
Melamine or Cyanuramide, $C_3N_4H_6=N_3 \left\{ \begin{array}{l} (C_3N_3) \\ H_6 \end{array} \right.$, is formed by polymerization of cyanamide when the latter is heated to 150° ; it is, however, more easily prepared by heating melam with potash-lye, the melam then being resolved into melamine and ammeline.

Melamine crystallizes in shining rhombic octohedrons, easily soluble in water, but insoluble in alcohol and ether. It forms well-crystallized salts containing 1 equivalent of acid, e. g., $C_3N_4H_6.HCl$. When boiled with acids or alkalis, it is converted successively, by assumption of H_2O and elimination of NH_3 , into ammeline, ammelide, and cyanuric acid.

Triethyl- and trimethyl-melamine are formed by polymerization of ethyl- and methyl-cyanamide, when the aqueous solutions of these bodies are evaporated. They are crystalline, strongly alkaline bodies, which are converted, by boiling with hydrochloric acid, into the corresponding derivatives of ammeline, and ultimately into isocyanuric ethers.

Ammeline, $C_3N_3H_5O = C_3N_3 \left\{ \begin{array}{l} OH \\ (NH_2)_2 \end{array} \right.$, is a white powder insoluble in water, alcohol, and ether, but soluble in acids and alkalis, and forming crystalline salts, which are decomposed by water.

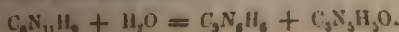
Ammelide, $C_3N_4H_4O_2 = C_3N_3 \left\{ \begin{array}{l} (OH)_2 \\ NH_2 \end{array} \right.$, is a white powder which dissolves in alkalis and in concentrated acids, but does not form definite salts with the latter. Its ammoniacal solution gives with silver nitrate a white precipitate having the composition



Melam, $C_6H_8N_{11}$, is a buff-colored, insoluble, amorphous substance, obtained by the distillation of ammonium thiocyanate at a high temperature. It may be prepared in large quantity by intimately mixing 1 part of perfectly dry potassium thiocyanate with 2 parts of powdered sal-ammoniac, and heating the mixture for some time in a retort or flask: carbon bisulphide, ammonium sulphide, and sulphuretted hydrogen, are disengaged and volatilized, while a mixture of melam, potassium chloride, and sal-ammoniac remains; the two latter substances are removed by washing with hot water. Melam dissolves in concentrated sulphuric acid, and gives, by dilution with water and long boiling, cyanuric acid. The same substance is produced, with disengagement of ammonia, when melam is fused with potassium hydrate. When strongly heated, melam is resolved into mellone and ammonia:—



and by prolonged boiling with moderation strong caustic potash, it is resolved into melamine and ammeline:—



Mellone and Mellonides.—The name mellone was given by Liebig to a yellow insoluble substance obtained as a residue in the decomposition of perthiocyanogen, or of melain, at a low red heat. The composition of the product thus obtained varies with the duration of the heating. If the decomposition be stopped at a certain point, the product has the composition of dicyanuramide, $N_2 \left\{ \begin{array}{l} (C_3N_3)''' \\ (C_3N_3)''' \\ H_3 \end{array} \right.$; but this, when further heated

still, gives off ammonia, and becomes continually richer in carbon, approaching, in fact, continually nearer to the composition of tricyanuramide, $C_6N_{12} = N_3(C_3N_3)_2$, which is probably the ultimate product of the decomposition, though it has never been actually attained; the product always containing a small quantity of hydrogen, however long the heating may be continued.

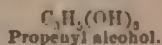
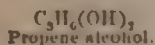
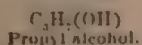
Mellone is also produced by ignition of ammonium thiocyanate and mercury thiocyanate. When boiled with nitric acid, it is resolved into ammonia and cyanuric acid.

Mellonides. $C_6N_{12}M_3$ (M denoting a monatomic positive radical).—*Tripotassic mellonide*, $C_6N_{12}K_3$, is produced by ignition of potassium thiocyanate, the preparation being greatly facilitated by the presence of a metallic compound, such as trichloride of antimony or bismuth, capable of taking up a portion of the sulphur which is set free as carbon sulphide. It may also be prepared by fusing potassium thiocyanate with crude mellone, or the ferrocyanide with half its weight of sulphur. The fused mass obtained by either process is dissolved in boiling water, from which the tripotassic mellonide crystallizes on cooling in silky needles, containing $C_6N_{12}K_3 + 5H_2O$, insoluble in alcohol and in ether. Acetic acid converts this salt into dipotassic mellonide, $C_6H_{12}K_2H$, which is also soluble. Hydrocyanic acid produces the *monopotassic salt*, $C_6N_{12}KH_2$, which is insoluble. These three salts stand to each other in the same relation as the several salts of phosphoric and cyanuric acids. Tripotassic mellonide produces, with soluble silver salts, a white precipitate, $C_6N_{12}Ag_3$; with lead salt and mercury salts, precipitates containing respectively $(C_6N_{12})_2Pb_3$ and $(C_6N_{12})_2Hg_3$. The latter, dissolved in hydrocyanic acid and treated with sulphuretted hydrogen, yields *hydromellonic acid*, $C_6N_{12}H_3$, which is known only in solution, has an acid taste, and is decomposed by evaporation into ammonia and mellone.

Cyamelurio Acid, $C_6N_7O_3H_3$.—The potassium salt of this acid is formed by boiling tripotassic mellonide with strong potash-lye, and the acid itself may be separated from the solution of the salt by a mineral acid in the form of a crystalline precipitate. It is a strong tribasic acid, converted by heating with mineral acids into cyanuric acid.

ALCOHOLS AND ETHERS.

The term alcohol, originally limited to one substance, viz., spirit of wine, is now applied to a large number of organic compounds, many of which, in their external characters, exhibit but little resemblance to common alcohol. They are all, however, analogously constituted, having the composition of hydrocarbons in which one or more of the hydrogen-atoms are replaced by hydroxyl; they may therefore be regarded as compounds of hydroxyl with univalent or multivalent hydrocarbon-radicles, hence called alcohol-radicles. Thus from propane C_3H_8 , are derived the three alcohols:—



Alcohols are accordingly classed as monatomic, diatomic, triatomic, etc., or generally as monatomic and polyatomic, according to the number of hydroxyl-groups which they contain, or according to the equivalent values of their hydrocarbon-radicles.

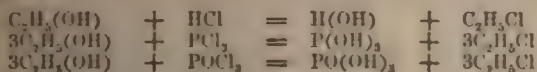
The replacement, partial or total, of the hydroxyl in an alcohol by chlorine, bromine, iodine, or fluorine, gives rise to haloïd ethers; thus:—

From $C_3H_7(OH)$ are derived C_3H_7Cl , C_3H_7Br , etc.

" $C_3H_6(OH)_2$ " $C_3H_5Cl(OH)$, $C_3H_5Cl_2$, etc.

" $C_3H_5(OH)_3$ " $C_3H_4Cl(OH)_2$, $C_3H_4Cl_2(OH)$, $C_3H_4Cl_3$, etc.

These substitutions are effected by treating the alcohols with the chlorides, bromides, and iodides of hydrogen or phosphorus, as in the following equations, which represent the formation of ethyl chloride from common alcohol:—



Instead of the bromides and iodides of phosphorus, the elements phosphorus and bromine or iodine, in the proportions required to form them, are often used in these processes.

These haloïd ethers are also formed in many instances by direct substitution of chlorine, bromine, etc., for hydrogen in saturated hydrocarbons, as explained in the preceding pages.

The treatment of the haloïd ethers with caustic aqueous alkalies gives rise to a substitution opposite to that exhibited in the above equations, converting the ethers into alcohols, *c. g.*—



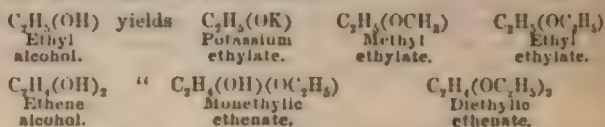
A considerable portion of the alcohol thus produced is, however, converted, by dehydration, into the corresponding olefine; *c. g.*: $C_2H_5O - H_2O = C_2H_4$. A better result is obtained by heating the haloïd ether with moist silver oxide, which acts like a hydroxide, $AgOH$. A still better method is to convert the alcoholic chloride, etc., into an acetate, by heating it with acetate of silver or potassium, and boil the resulting acetic ether with caustic potash or soda; thus:—



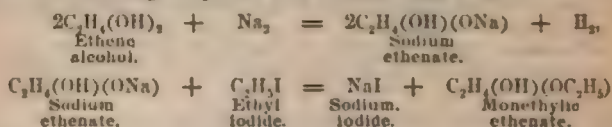
and



The replacement of the hydroxyl in an alcohol by the corresponding radicles, potassoxyl, OK, methoxyl, OCH_3 , ethoxyl, OC_2H_5 , etc. (p. 236), or of the hydrogen in the hydroxyl by potassium, methyl, ethyl, etc., gives rise to oxygen-ethers; thus:—

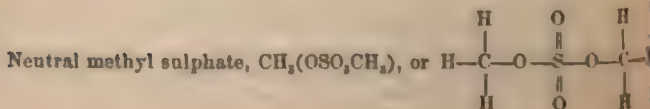
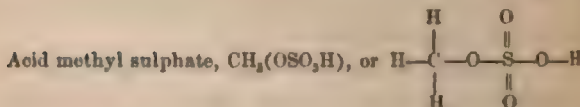
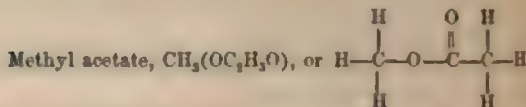
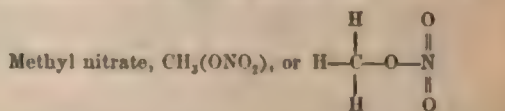


These substitutions may be effected in various ways. The simplest to replace an atom of hydrogen in the alcohol by potassium or sodium, act on the resulting compound with a haloid ether; thus:—

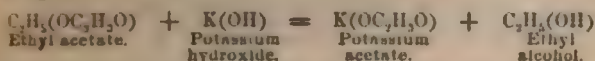


In the polyatomic alcohols, two hydroxyl groups may also be replaced by one atom of oxygen, giving rise to another class of oxygen ethers, thus from ethene alcohol, $\text{C}_2\text{H}_4(\text{OH})_2$, is derived ethene oxide, $\text{C}_2\text{H}_4\text{O}$.

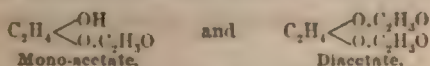
The replacement of the hydrogen of the hydroxyl in an alcohol by a radicle (p. 481), produces ethereal salts or compound ethers; thus, from methyl alcohol, $\text{CH}_3(\text{OH})$, are derived:—



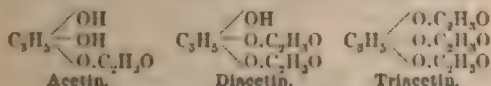
These ethereal salts may also be derived from the corresponding acids by substitution of alcohol-radicles for hydrogen, being in fact related to the alcohols in the same manner as metallic salts to metallic hydroxides. When distilled with alkalis, they are resolved into an acid and an alcohol; e. g.:



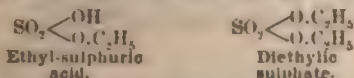
The number of compound ethers that can be formed by a given acid and alcohol depends upon the number of hydroxyl-groups which each of them contains, in other words, on their atomicity: thus, ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, and acetic acid, $\text{C}_2\text{H}_3\text{O}_2\text{OH}$, both of which are monatomic, yield but one ether, viz., ethyl acetate, $\text{C}_2\text{H}_5\text{O.O.C}_2\text{H}_3$; but ethene alcohol or glycol, $\text{H}_2(\text{OH})_2$, which is diatomic, forms two ethers with acetic acid, viz.:



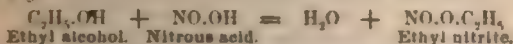
and glycerin, $\text{C}_3\text{H}_5(\text{OH})_3$, which is triatomic, forms three acetic ethers, viz.:



On the other hand, nitric acid, NO_2OH , which is monatomic, forms but one ethylic ether, viz., ethyl nitrate, $\text{NO}_2\text{O.C}_2\text{H}_5$; but sulphuric acid, $\text{O}_3(\text{OH})_2$, which is diatomic, forms two ethylic ethers, viz.:



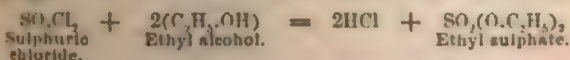
Compound ethers are formed: 1. By the action of the acids upon alcohols; e. g.:



This action takes place slowly at ordinary, more quickly at high temperatures, but the etherification is never complete, as the water separated in the process always exerts a reverse action on the ether, reconverting part of it into alcohol and acid.

Polybasic acids, acting upon alcohols, produce for the most part acid ethers.

2. By the action of chlorides of acid radicles on alcohols or their sodium derivatives.



3. By the action of haloïd ethers on the potassium or silver salts of the corresponding acids:



Neutral compound ethers are mostly volatile: the acid ethers are non-volatile, and as they still contain unreplaced hydrogen belonging to one

or more HO groups, they act as acids, exchanging this hydrogen for metals or for alcohol-radicles.

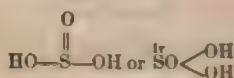
All compound ethers, but especially the acid ethers, are resolved into their components, alcohol and acid, by heating them with water, or more easily with potash or soda in aqueous or alcoholic solution :



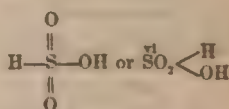
This process is called saponification, a term originally applied to the formation of soaps by boiling neutral fats (glycerin-ethers) with caustic alkali, but now extended to all similar decompositions.

Isomerism in the Compound Ethers.—The ethers of polybasic organic acids exhibit isomeric modifications, depending on the structure of the acid itself. The most important case of this kind of isomerism is presented by the sulphurous ethers.

Sulphurous acid is susceptible of two modifications, viz. :



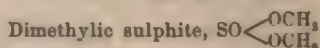
Symmetrical.



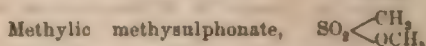
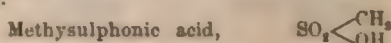
Unsymmetrical.

Both these modifications yield neutral alcoholic derivatives or sulphurous ethers, but only the unsymmetrical acid appears to form acid ethers, and these acid ethers are called sulphonic acids, *e. g.* :

Symmetrical :

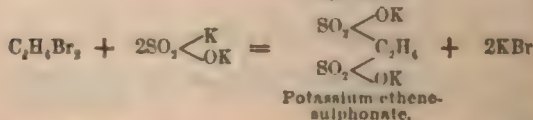
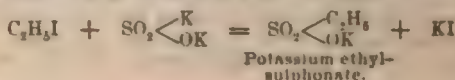


Unsymmetrical :

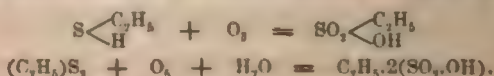


The sulphonic acids are formed by the following general reactions:—

1. By heating the haloid ethers to 120–150° C. (248°–302° F.) with a concentrated solution of potassium or sodium sulphite; thus :



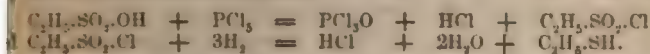
2. By oxidation of the hydrosulphides (mercaptans) and disulphides (also of the thiocyanates) of the alcohol radicles with nitric acid :



The mode of formation shows that the sulphur-atom of a sulphonic acid is directly united to the alcohol-radicle (and therefore to an atom of carbon), and hence it may be inferred, from the first reaction, that in the metallic sulphates an atom of metal is also directly united to the sulphur. The sulphonic acids are very stable compounds, not decomposed by boiling with caustic alkaline solutions. When fused with potassium hydroxide, however, they are resolved into an alcohol and sulphurous acid:



By the action of phosphorus pentachlorides they are converted into acid chlorides or chloranhydrides, which, by the action of nascent hydrogen, may be converted into mercaptans:



The ethers of the sulphonic acids are formed by the action of acid chlorides on the sodium-alcohols:



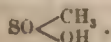
They are identical with the neutral ethers of unsymmetrical sulphurous acid, and may accordingly be also produced by the action of silver sulphite alcoholic iodides:



Analogous to the sulphonic acids are the sulphinic acids, or acid anhydrides of hyposulphurous acid, $SO \begin{smallmatrix} H \\ \diagup \\ OH \end{smallmatrix}$, the zinc salts of which are formed by the action of sulphur dioxide on the zinc compounds of the alcohol-radicles; e. g.:

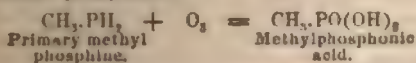


By converting the zinc salts into barium salts, and decomposing the latter with sulphuric acid, the free sulphinic acids are obtained as strongly volatile liquids which decompose when heated, e. g.:



The phosphorous ethers likewise exhibit isomeric modifications, derivable from symmetrical and unsymmetrical phosphorous acid $P(OH)_3$ and $HPO(OH)_2$. The neutral ethers of symmetrical phosphorous acid are formed by the action of phosphorous trichloride on the alcohols. The cyclic ether $P(O.C_2H_5)_3$, is a liquid boiling at $191^\circ C.$ ($275.8^\circ F.$).

Unsymmetrical phosphorous acid yields acid ethers called phosphonic acids, e. g., $(C_2H_5)PO \begin{smallmatrix} OH \\ \diagup \\ OH \end{smallmatrix}$, which are formed by the action of nitric acid on the primary phosphines:



They are crystalline bodies resembling spermaceti, dissolve in water, have a strong acid reaction, and act as bibasic acids, forming acid and neutral salts.

Hypophosphorous acid, $\text{H}_2\text{P.O.OH}$, yields analogous acid ethers, called phosphinic acids, which are formed by the action of nitric acid on the secondary phosphines; e. g.:



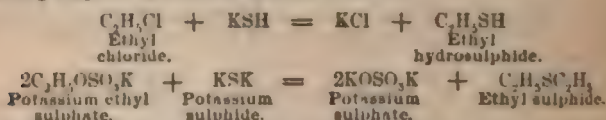
Arsenious acid, AsH_3O_2 , forms:

(a) *Symmetrical ethers*, like $\text{As}(\text{O.CH}_3)_3$, which are produced by the action of arsenious bromide, AsBr_3 , on the sodium alcohols; they are volatile without decomposition, and are resolved by water into arsenious acid and alcohols.

(b) *Unsymmetrical ethers*, called *arsonic acids*, analogous to the phosphonic acids, e. g., methylarsonic acid, $\text{CH}_3\text{AsO}(\text{OH})_2$; and lastly, there is a dimethylarsinic acid $(\text{CH}_3)_2\text{AsO.OH}$ (cacodylic acid), analogous to the phosphinic acids (see ARSENIC BASES.)

The nitrous ethers, as already observed, are isomeric with the nitroparaffins (p. 523).

The action of haloid ethers, or of certain ethereal salts, on the hydrosulphides and sulphides of the alkali-metals, gives rise to alcoholic hydrosulphides and sulphides, that is to say, alcohols and ethers containing sulphur in place of oxygen; thus:—



The alcoholic hydrosulphides, or thio-alcohols, are also called *mercaptans*, from their property of readily combining with mercury (*capere mercuria apti*). Their reactions are closely analogous to those of the oxygen-alcohols.

MONATOMIC ALCOHOLS AND ETHERS.

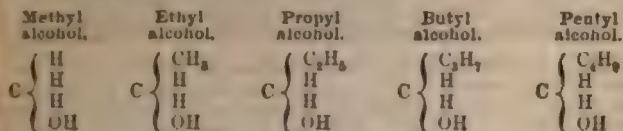
1. Containing the Radicles, $\text{C}_n\text{H}_{2n+1}$, homologous with Methyl.

The alcohols of this series are the best known and most important of all this class of bodies. They may be formed from the corresponding haloid ethers by the action of alkalies, and several of them are produced by the fermentation of sugar. There are also synthetical processes by which these alcohols may be built up in regular order, from the lowest upwards, but these will be better understood further on.

The names and formulæ of the known alcohols of this series are as follows:—

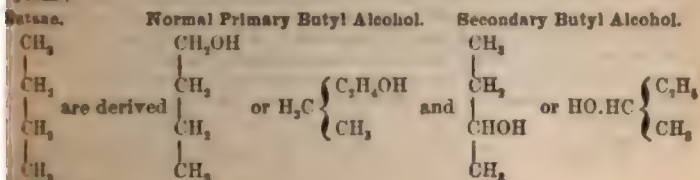
| | | | | | | | |
|----------------------------|---|---|---|---|---|---|--------------------------------------|
| Methyl alcohol | . | . | . | . | . | . | CH_3O |
| Ethyl alcohol | . | . | . | . | . | . | $\text{C}_2\text{H}_5\text{O}$ |
| Propyl alcohol | . | . | . | . | . | . | $\text{C}_3\text{H}_7\text{O}$ |
| Butyl alcohol | . | . | . | . | . | . | $\text{C}_4\text{H}_9\text{O}$ |
| Pentyl or Amyl alcohol | . | . | . | . | . | . | $\text{C}_5\text{H}_{11}\text{O}$ |
| Hexyl alcohol | . | . | . | . | . | . | $\text{C}_6\text{H}_{13}\text{O}$ |
| Heptyl alcohol | . | . | . | . | . | . | $\text{C}_7\text{H}_{15}\text{O}$ |
| Octyl alcohol | . | . | . | . | . | . | $\text{C}_8\text{H}_{17}\text{O}$ |
| Nonyl alcohol | . | . | . | . | . | . | $\text{C}_9\text{H}_{19}\text{O}$ |
| Hexadecyl or Cetyl alcohol | . | . | . | . | . | . | $\text{C}_{16}\text{H}_{33}\text{O}$ |
| Ceryl alcohol | . | . | . | . | . | . | $\text{C}_{21}\text{H}_{43}\text{O}$ |
| Melissyl alcohol | . | . | . | . | . | . | $\text{C}_{20}\text{H}_{41}\text{O}$ |

The formula of methyl alcohol is that of methane or marsh-gas having one atom of hydrogen replaced by hydroxyl; and the rest may be derived from it by replacement of one or more of the other hydrogen-atoms by methyl and its homologues. If we replace only one atom of hydrogen in this manner we obtain the series:—

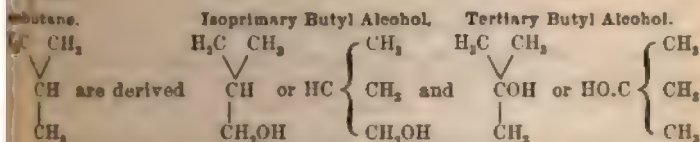


Now it is clear that, so long as the type of an alcohol is preserved—that is, of a hydrocarbon having at least one hydrogen-atom replaced by hydroxyl—the first two alcohols of this series do not admit of any other mode of formulation: in other words, they are not susceptible of isomeric modifications. But the higher members of the series admit of isomeric modifications analogous to those of the haloid ethers already mentioned (p. 496), and distinguished by similar names, an alcohol being designated as primary, secondary, or tertiary, according as the carbon-atom which is in combination with hydroxyl, is likewise directly united to one, two, or three other carbon-atoms. Moreover, the four-carbon-alcohol admits all above it in the series, admit of further modifications, according to the structure of the radicles (*normal* or *iso*) contained in them—all these modifications, like those of the haloid ethers, depending upon the structure of the paraffins from which the alcohols are derived; thus—

From:



and from



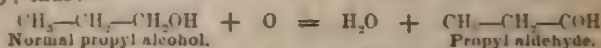
The primary alcohols are formed by substitution of OH for H in a methyl-group CH_3 ; the secondary and tertiary alcohols by similar substitution in a methane group CH_2 , and a methenyl-group respectively.

A very convenient nomenclature for these isomeric alcohols has been proposed by Kolbe. Methyl alcohol, $\text{CH}_3(\text{OH})$, is called carbinol; and the alcohols formed from it by successive substitution of methyl, ethyl, &c., for an atom of hydrogen, are named according to the radicles which they contain;* thus—

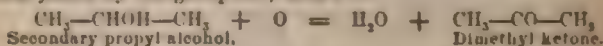
* Odling modifies this nomenclature by restricting the term carbinol to the primary alcohols, designating the secondary alcohols as pseudo-alcohols or pseudols, and employing the term alcohol especially to designate the

| | |
|---|----------------------|
| Carbinol, or Methyl alcohol | $C(OH)H_3$ |
| Methyl carbinol, or Ethyl alcohol | $C(OH)H_2C_2H_5$ |
| Ethyl carbinol, or Propyl alcohol | $C(OH)H_2C_3H_7$ |
| Dimethyl carbinol, or Pseudopropyl alcohol | $C(OH)H(C_2H_5)_2$ |
| Propyl carbinol, or Butyl alcohol | $C(OH)H_2(C_2H_5)_2$ |
| Isopropyl carbinol, or Isobutyl alcohol | $C(OH)H_2CH(CH_3)_2$ |
| Methyl-ethyl carbinol, or Secondary Butyl alcohol | $C(OH)H(C_2H_5)_2$ |
| Trimethyl carbinol, or Tertiary Butyl alcohol | $C(OH)(CH_3)_3$ |

Primary, secondary, and tertiary alcohols are distinguished from one another by the products which they yield by oxidation. Primary alcohols of the series $C_nH_{2n+2}O$, containing the group CH_2OH , are converted by oxidation with chromic acid, first into the corresponding aldehydes $C_nH_{2n}O$ by removal of H_2 , or conversion of the group CH_2OH into CHO , and then by further oxidation into the corresponding acids $C_nH_{2n}O_2$ (fatty acids); thus:—

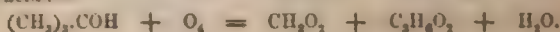


A secondary alcohol, on the other hand, which contains two alcohol-radicles united by the group $CHOH$, is converted, by removal of H , from this group, into a ketone, which is a compound consisting of two alcohol-radicles joined by the group CO ; thus:—



Conversely, the aldehydes treated with nascent hydrogen (action of sodium amalgam) are converted into primary alcohols, and the ketones by similar treatment into secondary alcohols.

Tertiary alcohols do not yield by oxidation either aldehydes, ketones, or acids containing the same number of carbon-atoms as the alcohols themselves, but are split up into compounds containing a smaller number of carbon-atoms; tertiary butyl alcohol, for example, into formic and propionic acid:—



METHYL ALCOHOL AND ETHERS.

Methyl Alcohol, Hydroxymethane, Carbinol, Methol, CH_3O or $CH_3(OH)$.—This is the simplest member of the series. It is produced:—

alcohols, proper or primary alcohols, which may also be called methols; thus—

| | | |
|---------------------|---|---|
| | Propyl Alcohol
or Ethyl-Methol. | Isobutyl Alcohol
or Isopropyl-Methol. |
| Primary | $H_2C \begin{Bmatrix} CH_2OH \\ CH_3 \end{Bmatrix}$ | $HC \begin{Bmatrix} CH_2OH \\ CH_3 \\ CH_3 \end{Bmatrix}$ |
| | Dimethyl Pseudol. | Ethyl-Methyl
Pseudol. |
| Secondary | $HOCH \begin{Bmatrix} CH_3 \\ CH_3 \end{Bmatrix}$ | $HOHC \begin{Bmatrix} CH_3 \\ CH_3 \end{Bmatrix}$ |
| | Trimethyl Carbinol. | Ethyl-Dimethyl
Carbinol. |
| Tertiary | $HO.C \begin{Bmatrix} CH_3 \\ CH_3 \\ CH_3 \end{Bmatrix}$ | $HO.C \begin{Bmatrix} CH_3 \\ CH_3 \\ CH_3 \end{Bmatrix}$ |

1. From marsh-gas, by subjecting that compound to the action of chlorine in sunshine, whereby chloromethane, or methyl chloride, CH_3Cl , is produced, and distilling with potash.

2. From wintergreen oil, which consist chiefly of acid methyl salicylate, $\text{C}_7\text{H}_5\text{O}_2, \text{H}.\text{CH}_3$, by distillation with potash, whereby potassium salicylate is formed, and methyl alcohol distils over:—



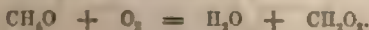
This reaction, which consists in the interchange of methyl and potassium, yields very pure methyl alcohol.

3. From crude wood-vinegar, the watery liquid obtained by the destructive distillation of wood: it was in this liquid that methyl alcohol was first discovered by P. Taylor, in 1812: hence it is often called *wood-spirit*. Crude wood-vinegar probably contains about $\frac{1}{100}$ part of methyl alcohol, which is separated from the great bulk of the liquid by distilling it, and drawing apart the first portions which pass over. The acid solution thus obtained is neutralized with slaked lime, and the clear liquid, separated from the oil which floats on the surface, and from the sediment at the bottom is again distilled. A volatile liquid is thus obtained, which burns like weak spirit; this may be strengthened by rectification, and ultimately rendered pure and anhydrous by careful distillation from quicklime at the bottom of a water-bath.

Pure methyl alcohol is a thin, colorless liquid, very similar in smell and taste to ethyl alcohol: crude wood-spirit, on the other hand, which contains many impurities, has an offensive odor and a nauseous, burning taste. Methyl alcohol boils at 66.6°C . (151.9°F .), and has a density of 0.798 at 0°C . (32°F .). Vapor-density (referred to hydrogen) = 16. Methyl alcohol when pure mixes in all proportions with water: it dissolves resins and volatile oils as freely as ethyl alcohol, and is often substituted for ethyl alcohol in various processes in the arts. It may be burnt instead of ordinary spirit in lamps: the flame is pale-colored, like that of ethyl alcohol, and deposits no soot. Methyl alcohol dissolves caustic baryta: the solution deposits, by evaporation in a vacuum, acicular crystals, containing $10.2\text{CH}_3\text{O}$. It dissolves calcium chloride in large quantity, and gives rise to a crystalline compound containing $\text{CaCl}_2, 2\text{CH}_3\text{O}$.

Potassium and sodium dissolve in it, with evolution of hydrogen yielding potassium and sodium methylates, CH_3OK , and CH_3ONa .

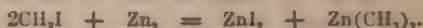
By oxidation, as by exposure to the air in contact with platinum black, it is converted into formic acid, CH_2O_2 , which is derived from it by substitution of 1 atom of oxygen for 2 atoms of hydrogen:



Methyl Chloride, or **Chloromethane**, CH_3Cl , is formed when a mixture of equal volumes of methane (marsh-gas) and chlorine is exposed to direct sunlight. It is more easily prepared, however, by heating a mixture of 2 parts of common salt, 1 part of wood-spirit, and 3 parts of concentrated sulphuric acid. It is a gaseous body, which may be conveniently collected over water, as it is but slightly soluble in that liquid. It is colorless; has a peculiar odor and sweetish taste, and burns, when ignited, with a pale flame, greenish towards the edges, like most combustible chlorine-compounds. Its density, referred to hydrogen as unity, is 2.25; it is not liquefied at -18°C . (0.4°F .). The gas is decomposed by transmission through a red-hot tube, with slight deposition of carbon, into hydrochloric acid gas and a hydrocarbon which has been but little examined. By the action of chlorine in sunshine it is successively converted into *methene chloride*, or *dichloromethane*, CH_2Cl_2 , a liquid boiling at

30.5° C. (86.9° F.); *methenyl chloride*, *trichloromethane*, or *chloroform*, CHCl_3 , and *carbon tetrachloride*, CCl_4 .

Methyl Iodide, or **Iodomethane**, CH_3I , is a colorless and feebly combustible liquid, obtained by distilling together 1 part of phosphorus, iodine, and 12 or 15 of methyl-alcohol. It is insoluble in water, has a density of 2.237, and boils at 44° C. (111.2° F.). The density of vapor, referred to hydrogen as unity, is 71. When digested in sealed tubes with *zinc*, it yields a colorless gaseous mixture containing ethane, or *ethyl*, C_2H_6 , and the residue contains zinc iodide, together with zinc methyl $\text{Zn}(\text{CH}_3)_2$:



Methyl Ether, **Methyl Oxide**, or **Methoxyl-methane**, $\text{C}_2\text{H}_6\text{O}$, $(\text{CH}_3)_2\text{O} = \text{C} \begin{Bmatrix} \text{H}_3 \\ \text{OCH}_3 \end{Bmatrix}$.—This compound, which bears the same relation to methyl alcohol that anhydrous potassium oxide bears to potassium hydroxide, is produced by abstraction of the elements of water from methyl alcohol: $2\text{CH}_3\text{O} - \text{H}_2\text{O} = \text{C}_2\text{H}_6\text{O}$.

It may be prepared by heating 1 part of methyl-alcohol and 4 parts of concentrated sulphuric acid, and passes over as a colorless gas, which may be collected over mercury. It does not liquefy at -16° C. (3.2° F.). It has an ethereal odour, and burns with a pale and feebly-luminous flame. Its specific gravity is 1.617 referred to air, or 23 referred to hydrogen as unity. Cold water dissolves about 33 times its volume of this gas, acquiring thereby its characteristic taste and odor; on boiling the solution, the gas is again liberated. Alcohol, wood-spirit, and concentrated sulphuric acid dissolve it in still larger quantity.

Methyl Nitrate, $\text{CH}_3.\text{NO}_3$, or $\text{CH}_3.\text{O}.\text{NO}_3$. This ether is obtained by distilling 50 grams of pounded nitre with 50 grams of methyl alcohol and 100 grams of sulphuric acid, in a retort without external heating. It is a colorless liquid of sp. gr. 1.182 at 20° C. (68° F.); boils at 60° C. (140° F.) and has a faint ethereal odor. Its vapor detonates violently when heated above 150° C. (302° F.). Heated with *alcoholic ammonia*, it yields methyl ammonium nitrate, $\text{CH}_3\text{N}.\text{NO}_3\text{H}$. Distilled with aqueous *potash*, it yields methyl ethoxide.

Methyl Nitrite, $\text{CH}_3.\text{O}.\text{NO}$, isomeric with nitromethane, $\text{CH}_3.\text{NO}_2$ (524), is produced by the action of nitrous acid on methyl alcohol. It is a gas having a pleasant odor, and condensing at very low temperatures into a yellowish liquid which boils at -12° C. (10.4° F.).

Methyl Sulphates.—Sulphuric acid, being a bibasic acid, yields two methyl ethers—one acid, the other neutral.

Acid Methyl sulphate, *Methyl and Hydrogen sulphate*, *Methylsulphuric acid*, or *Sulphomethylic acid*, $\text{CH}_3.\text{H}.\text{SO}_4$, or $\text{SO}_4 \begin{Bmatrix} \text{OCH}_3 \\ \text{OH} \end{Bmatrix}$.—To prepare this acid ether, 1 part of methyl alcohol is slowly mixed with two parts of concentrated sulphuric acid, and the whole is heated to boiling, and then cooled, after which it is diluted with water, and neutralized with barium carbonate. The solution is filtered from the insoluble sulphate, and evaporated, first in a water-bath, and afterwards in a vacuum to the proper degree of concentration. The salt crystallizes in beautiful, square, colorless tables, containing $(\text{CH}_3)_2\text{Ba}(\text{SO}_4)_2.2\text{H}_2\text{O}$, which effloresce in dry air, and are very soluble in water. By exactly precipitating the base with

this substance with dilute sulphuric acid, and leaving the filtered liquid to evaporate in the air, methylsulphuric acid may be procured in the form of a sour, syrupy liquid, or in minute acicular crystals, very soluble in water and alcohol. It is very instable, being easily decomposed by heat.

Potassium methylsulphate, CH_3KSO_4 , crystallizes in small, nacreous, deliquescent rhombic tables. The *lead salt* is also very soluble.

Neutral Methyl sulphate, or *Dimethyl sulphate* $(\text{CH}_3)_2\text{SO}_4$, or $\text{SO}_2(\text{OCH}_3)_2$.—This ether is prepared by distilling 1 part of methyl alcohol with 8 or 10 parts of strong sulphuric acid: the distillation may be carried nearly to dryness. The oleaginous liquid found in the receiver is agitated with water, and purified by rectification from powdered anhydrous baryta. The product is a colorless, oily liquid, of alliacious odor, having a density of 1.524, and boiling at 188°C . (370.4°F). It is neutral to test-paper, and insoluble in water, but decomposed by that liquid, slowly in the cold, rapidly and with violence at a boiling temperature, into methylsulphuric acid and methyl alcohol. Anhydrous lime and baryta have no action on this ether: their hydrates, however, and those of potassium and sodium, decompose it instantly, with production of a methylsulphate of the base, and methyl alcohol. When neutral methylsulphate is heated with common salt, it yields sodium sulphate and methyl chloride; with mercuric cyanide, or potassium cyanide, it gives a sulphate of the base and methyl cyanide; with dry sodium formate, it yields sodium sulphate and methyl formate.

Methyl Sulphite (symmetrical), $\text{SO}(\text{O.CH}_3)_2$, formed by the action of sulphur dichloride, S_2Cl_2 , on methyl alcohol, as a fragrant liquid having a specific gravity of 1.045, and boiling at 121°C . (249.8°F).

Methylsulphonic Acid, $\text{CH}_3\text{SO}_3\text{H}$, is prepared by heating methyl sulphite with a concentrated solution of potassium or sodium sulphite, converting the resulting methylsulphonate into a lead-salt, decomposing the latter with hydrogen sulphide, and evaporating the filtered solution. The acid then remains as a viscid, uncrystallizable liquid, soluble in water. Its salts are easily soluble in water, and crystallize well; the barium salt, $(\text{CH}_3\text{SO}_3)_2\text{Ba}$, in rhombic plates.

Methylsulphonic Chloride, $\text{CH}_3\text{SO}_3\text{Cl}$, boils at 153°C . (307.4°F), and is decomposed by water into hydrochloric and methylsulphonic acids.

Trichloromethylsulphonic Chloride, $\text{CCl}_3\text{SO}_3\text{Cl}$, is formed by the action of moist chlorine on carbon bisulphide. To prepare it, a mixture of 500 grams of hydrochloric acid, 300 grams of coarsely pounded potassium dichromate, 200 grams of nitric acid, and 30 grams of carbon bisulphide is left to itself in an open flask for about a week, water is added, and the crystals of the compound, CCl_3SO_3 , are separated from the saline solution by filtration.

The chloride or chloranhydride thus formed is a colorless crystalline body, which melts at 135°C . (275°F), and boils at 170°C . (338°F). It has a camphorous tear-exciting odor, dissolves in alcohol and ether, but is insoluble in water.

Trichloromethylsulphonic Acid, $\text{CCl}_3\text{SO}_3\text{H}$, is obtained by boiling the chloride just described with baryta-water, and decomposing the resulting barium salt with sulphuric acid. It crystallizes in deliquescent prisms; the barium salt, $(\text{CCl}_3\text{SO}_3)_2\text{Ba} + \text{H}_2\text{O}$, in laminae.

This trichlorinated acid heated in aqueous solution with sodium-amalgam is converted successively into the acids, $\text{CHCl}_2\text{SO}_3\text{H}$, $\text{CH}_2\text{ClSO}_3\text{H}$, and finally into methylsulphonic acid, $\text{CH}_3\text{SO}_3\text{H}$. This series of reactions, discovered by Kolbe in 1845, afforded one of the earliest instances of the formation of an organic compound from inorganic materials.

into methylphosphonic chloride, $(\text{CH}_3)_2\text{POCl}_2$, which melts (89.6° F.), boils at 163° C. (325.4° F.), and is reconverted into methyl alcohol by the action of water.

Dimethylphosphinic acid, $(\text{CH}_3)_2\text{PO.OH}$, is a mass of paraffin, melting at 76° C. (168.8° F.), and volatilizing without decomposition.

On *Methyl-arsonic and Methyl-arsinic Acids*, see ARSENIC BASES.

Methyl Silicate, $\text{Si}(\text{OCH}_3)_4$, is obtained by acting upon potash and dry methyl alcohol with silicon tetrachloride, and distilling the product. It is a colorless liquid, of pleasant, ethereal odor, specific gravity 1.0589 at 0°, distilling between 121° and 126° C. (249.8° and 258.8° F.). It dissolves with moderate facility in water, and the solution does not become turbid, from separation of silica, for some weeks. Its vapor-density is 5.38 referred to air, or 77.6 referred to hydrogen, calculated number being 76.

Methyl Hydrosulphide, CH_3SH , also called **Methyl Mercaptan**, This compound, which has the composition of methyl alcohol, the oxygen replaced by sulphur, is formed by distilling in a water-bath a mixture of calcium methylsulphate and calcium hydrosulphide:



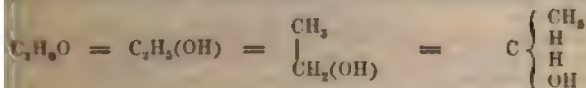
It is a liquid lighter than water, and having an extremely offensive odor. It forms with lead-acetate a yellow precipitate, and with mercurous chloride a white compound, $(\text{CH}_3)_2\text{S}_2\text{Hg}$, which crystallizes from alcohol in thin laminae.

Methyl Sulphide, $(\text{CH}_3)_2\text{S}$, or $\text{H}_3\text{C}-\text{S}-\text{CH}_3$, is obtained by acting on gaseous methyl chloride into a solution of potassium monochloride in methyl alcohol. It is a colorless, mobile, fetid liquid, of specific gravity 0.845 at 21° C. (69.8° F.), boiling at 41° C. (105.8° F.). It for

ethyl Telluride, or Telluro-methyl, $(\text{CH}_3)_2\text{Te}$, obtained by distilling potassium telluride with potassium methylsulphate, is an oily fetid compound resembling ethyl telluride, which will be described hereafter. The corresponding selenium-compound has also been obtained.

ETHYL ALCOHOL AND ETHERS.

Ethyl Alcohol, Hydroxyl-ethane, or Methyl Carbonol,



Important compound, the oldest and best known of the whole group of alcohols, and generally designated by the simple name "alcohol," is ethyl alcohol:—

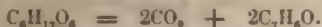
from ethene, C_2H_4 , by addition of the elements of water. When the gas and strong sulphuric acid are violently agitated together for a time, the gas is absorbed, and ethylsulphuric acid, $\text{C}_2\text{H}_5\text{SO}_4$, is produced, and this compound, distilled with water, yields sulphuric acid and ethyl alcohol:—



As we have seen that ethene can be formed by addition of hydrogen to acetylene, C_2H_2 , which is itself formed by direct combination of carbon and hydrogen. It follows, therefore, that alcohol can be produced synthetically from the elements.

from ethyl chloride, bromide or iodide by the reactions mentioned (p. 515).

by the fermentation of certain kinds of sugar. When a moderate warm solution of cane-sugar or grape-sugar (glucose) is mixed with albuminous matters, as blood, white of egg, flour-paste, and especially beer-yeast, in a state of decomposition, a peculiar process, called *fermentation*, is set up, by which the sugar is resolved into ethyl alcohol and carbon dioxide. In the case of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, these products result from the splitting up of the molecule:—



Sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is first converted into glucose by assumption of water, $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} = 2\text{C}_6\text{H}_{12}\text{O}_6$, and the latter is then decomposed as above.*

Ordinary cane-sugar be dissolved in a large quantity of water, a due portion of active yeast added, and the whole maintained at a temperature of $21^\circ\text{--}26^\circ\text{C}$. ($70^\circ\text{--}80^\circ\text{F}$.), the change will go on with great rapidity. The gas disengaged is nearly pure carbon dioxide: it is easily collected and examined, as the fermentation, once commenced, proceeds perfectly in a close vessel, such as a large bottle or flask fitted with a cork and a delivery tube. When the effervescence is at an end, and the liquid becomes clear, it will yield alcohol by distillation.

In addition to this principal decomposition, a variety of other changes are occasionally accomplished. According to Pasteur, glycerin, succinic acid, cellosol, and occasionally lactic acid, are observed among the products of alcohol-fermentation. Some of the homologues of ethyl alcohol are also found among the products.

The spirit first obtained by distilling a fermented saccharine liquid is very weak, being diluted with a large quantity of water. By a second distillation, in which the first portions of the distilled liquid are collected apart, it may be greatly strengthened: the whole of the water can, however, be thus removed. The strongest rectified spirit of wine of commerce has a density of about 0.835, and yet contains 13 or 14 per cent water. Pure or *absolute* alcohol may be obtained from it by redistilling with half its weight of fresh quicklime. The lime is reduced to a powder, and put into a retort; the alcohol is added, and the whole mixed by agitation. The neck of the retort is securely stopped with a cork, the mixture left for several days. The alcohol is distilled off by the use of a water-bath.

Pure alcohol is a colorless, limpid liquid, of pungent and agreeable taste and odor; its specific gravity, at 15.5° C. (60° F.), is 0.7938, and the vapor, referred to air, 1.613. It is very inflammable, burning with a pale bluish-flame, free from smoke; it has never been frozen. Alcohol boils at 78.4° C. (173° F.) when in the anhydrous state; in a diluted state the boiling point is higher, being progressively raised by each addition of water. In the act of dilution a contraction of volume occurs, and the temperature of the mixture rises many degrees: this takes place not only with pure alcohol, but also with rectified spirit. Alcohol is miscible with water in all proportions, and, indeed, has a great attraction for the latter, absorbing its vapor from the air, and abstracting the moisture from a variety of anhydrous and other similar substances immersed in it. The solvent powers of alcohol are very extensive; it dissolves a great number of saline substances, and likewise a considerable proportion of potash. With the salts it forms definite crystalline compounds, called *alcoholates*: with zinc chloride, $\text{ZnCl}_2 \cdot 2\text{C}_2\text{H}_5\text{O}$; with calcium chloride, $\text{CaCl}_2 \cdot 4\text{C}_2\text{H}_5\text{O}$; with magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{C}_2\text{H}_5\text{O}$. Alcohol dissolves, moreover, many organic substances, as the vegetable alkalies, resins, essential oils, and various other bodies: hence its great use in chemical investigations and in several of the arts.

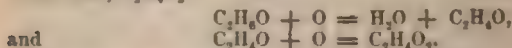
Potassium and sodium dissolve in ethyl alcohol in the same manner as in methyl alcohol, forming the compounds $\text{C}_2\text{H}_5\text{KO}$ and $\text{C}_2\text{H}_5\text{NaO}$.

Alcohol, passed through a red-hot tube, is resolved into marsh-gas, hydrogen, and carbon monoxide.



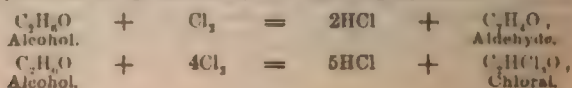
Small quantities of ethene, benzene, and naphthaline are, however, formed at the same time by the mutual action of these primary products, and carbon is deposited.

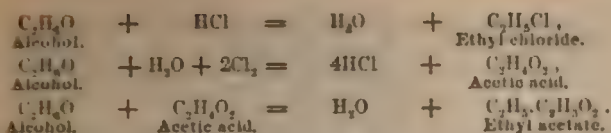
By *oxidation*, alcohol is converted first into aldehyde, $\text{C}_2\text{H}_4\text{O}$, then into acetic acid, $\text{C}_2\text{H}_4\text{O}_2$:



and

Chlorine gas is rapidly absorbed by anhydrous alcohol, turning it yellow and causing considerable rise of temperature. At the same time it rapidly abstracts hydrogen, which is partly replaced by the chlorine, producing hydrochloric acid, aldehyde, acetic acid, ethyl acetate, ethyl chloride, chloral. The mixture of these substances, freed by water from the solvent constituents, was formerly called *heavy muriatic ether*. The formation of several products is represented by the following equations:—





When the action of the chlorine is continued for a long time, chloral is always the principal product. This compound is a heavy oily liquid, having the composition of aldehyde with 3 atoms of hydrogen replaced by chlorine; but it cannot be formed by the direct action of chlorine upon aldehyde. When alcohol containing water is used, scarcely any chloral is obtained, the chief product being aldehyde.

Chlorine, in presence of *alkalies*, converts alcohol into chloroform, CHCl_3 , carbon dioxide:—



The same products are formed by distilling dilute alcohol with bleaching-powder.

Aqueous alcohol heated with strong *sulphuric acid* is converted into ethyl-sulphuric acid, $\text{C}_2\text{H}_5\text{SO}_4$; but when anhydrous alcohol is exposed to the action of sulphuric oxide, SO_3 , a white crystalline substance is formed, called *ethionie oxide*, formerly *sulphate of carbyl*, $\text{C}_2\text{H}_5\text{S}_2\text{O}_6$. This, when dissolved in water or in aqueous alcohol, is converted into *ethionie acid*, $\text{C}_2\text{H}_5\text{S}_2\text{O}_7$, a dibasic acid, which forms a soluble barium salt. Lastly, *ethionie acid*, when boiled, is resolved into sulphuric acid and *isethionie acid*, an acid isomeric with ethyl-sulphuric acid.

Commercial Spirit, Wine, Beer, etc. Vinous Fermentation.—The strength of commercial spirit, when free from sugar and other substances added frequently to distillation, is inferred from its density: a table exhibiting the proportions of real alcohol and water in spirits of different densities will be found at the end of the volume. The *excise proof spirit* has a specific gravity of 0.9198 at 60° F., and contains 49½ per cent. by weight of real alcohol.

The high duty on spirits of wine in this country has hitherto interfered with the development of many branches of industry, which are dependent on the free use of this important liquid. The labors of the scientific chemists have been likewise often checked by this inconvenience. A remedy for this evil has been supplied by a very important measure, proposed and carried out by the late Mr. John Wood, Chairman of the Board of Inland Revenue. This measure consists in issuing, for manufacturing and scientific purposes, duty free, a mixture of 90 per cent. of spirits of wine of strength not less than corresponds with a density of 0.830, and 10 per cent. of partially purified wood-spirit, which is now sold by licensed dealers under the name of *Methylated Spirit*. It appears that a mixture of this kind is rendered permanently unfit for human consumption, the separation of the two substances, in consequence of their close analogy, being not only difficult, but to all appearance impossible: at the same time, for the same reasons, this mixture is not materially impaired for the greater number of the more valuable purposes in the arts for which spirits are usually employed. Methylated spirit may be used, instead of pure spirit, as a solvent of resinous substances, and of many chemical preparations, especially of the alkaloids and other organic products. It may be used for the production of fulminating mercury, ether, chloroform, iodo-

form, olefant gas, and all its derivatives—in fact, for an endless number of laboratory purposes. Methylated spirit may also be substituted for pure spirit of wine in the preservation of anatomical preparations. The introduction of this spirit has already exerted a very beneficial effect upon the development of organic chemistry in England.*

Wine, Beer, etc., owe their intoxicating properties to the alcohol they contain, the quantity of which varies very much. Port and sherry, and some other strong wines, contain from 19 to 25 per cent. of alcohol, while in the lighter wines of France and Germany it sometimes falls as low as 12 per cent. Strong ale contains about 10 per cent.; ordinary spirits, of brandy, gin, whiskey, 40 to 50 per cent., or occasionally more. These latter owe their characteristic flavors to certain essential oils and compound ethers, present in very small quantity, either generated in the act of fermentation or purposely added.

In making wine, the expressed juice of the grape is simply set aside in large vats, where it undergoes spontaneously the necessary change. The vegetable albumin of the juice absorbs oxygen from the air, runs into decomposition, and in that state becomes a ferment to the sugar, which is gradually converted into alcohol. If the sugar be in excess, and the azotized matter deficient, the resulting wine remains sweet; but if, on the other hand, the proportion of sugar be small and that of albumin large, a *dry* wine is produced. When the fermentation stops, and the liquor becomes clear, it is drawn off from the lees, and transferred to casks, to ripen and improve.

The color of red wine is derived from the skins of the grapes, which in such cases are left in the fermenting liquid. Effervescent wines, as champagne, are bottled before the fermentation is complete; the carbonic acid is disengaged under pressure, and retained in solution in the liquid. A certain quantity of sugar is frequently added. The process requires much delicate management.

During the fermentation of the grape-juice, or *must*, a crystalline, stony matter, called *argol*, is deposited. This consists chiefly of acid potassium tartrate with a little coloring matter, and is the source of all the tartaric acid met with in commerce. The salt in question exists in the juice in considerable quantity; it is but sparingly soluble in water, but still less so in dilute alcohol; hence, as the fermentation proceeds, and the quantity of spirit increases, it is slowly deposited. The acid of the juice is thus removed as the sugar disappears. It is this circumstance which renders grape-juice alone fit for making good wine; when that of gooseberries or currants is employed as a substitute, the malic and citric acid which these fruits contain cannot be thus withdrawn. There is then no other resource but to add sugar in sufficient quantity to mask and conceal the natural acidity of the liquor. Such wines are necessarily astringent, prone to a second fermentation, and, to many persons at least, very unwholesome.

Beer is a well-known liquor, of great antiquity, prepared from germinated grain, generally barley, and is used in countries where the vine does not flourish. The operation of *malting* is performed by steeping the barley in water until the grains become swollen and soft, then piling it in a heap or *couch*, to favor the rise of temperature caused by the absorption of oxygen from the air, and afterwards spreading it upon a floor, and turning it over from time to time to prevent unequal heating. When germination has proceeded far enough, the vitality of the seed is destroyed by kiln-drying.

* See Report on the Supply of Spirits of Wine, free from duty, for use in the Arts and Manufactures, addressed to the Chairman of Inland Revenue by Professors Graham, Hofmann, and Redwood. (Quarterly Journal of Chemical Society, vol. viii. p. 120.)

This process, a peculiar nitrogenous substance called *diastase* is used, which acts as a ferment on the starch of the grain, converting it into sugar and rendering it soluble.

Following, the crushed malt is infused in water at about 77°C . (1700°F) the mixture is left to stand for two hours or more. The easily soluble *diastase* has thus an opportunity of acting upon the unaltered starch of the grain, and changing it into dextrin and sugar. The clear *wort*, strained from the exhausted malt, is next pumped up into a boiler, and boiled with the requisite quantity of hops, to communicate a pleasant bitter flavor, and confer on the beer the property of keeping without injury. The flowers of the hop contain a bitter, resinous substance, called *lupulin*, and an essential oil.

As the wort has been sufficiently boiled, it is drawn from the copper, and cooled as rapidly as possible, to near the ordinary temperature of the air, in order to avoid an irregular acid fermentation, to which it would be liable. It is then transferred to the fermenting vessels, which in large breweries are of great capacity, and mixed with a quantity of the product of a preceding operation, by which the change is induced. This is the most critical part of the whole operation, in which the skill and judgment of the brewer are most called in for. The process is in some measure under control by attention to the temperature of the liquid; and the extent to which the change has proceeded is easily known by the diminished density, or *attenuation* of the liquid. The fermentation is never suffered to run its full course, but is stopped at a particular point, by separating the yeast, and drawing the beer into casks. A slow and almost insensible fermentation succeeds, which in time renders the beer stronger and less sweet than when first charged it with carbonic acid.

For colored beer is made by adding to the malt a small quantity of dried or charred malt, the sugar of which has been changed to malt sugar; porter and stout are so prepared.

The yeast of beer is a very remarkable substance. To the naked eye it is a cream-yellow soft solid, nearly insoluble in water, and dries up to a brownish mass, which readily putrefies when moistened, and becomes offensive. Under the microscope it exhibits a kind of organic appearance, being made up of little transparent globules, which cohere in clusters or strings, like some of the lowest members of the vegetable kingdom. Whatever may be the real nature of the substance, no doubt can exist that it is formed from the soluble azotized portion of the grain during the fermentative process. No yeast is ever produced in liquids free from azotized matter; that added for the purpose of fermentation in pure sugar is destroyed, and rendered inert. When yeast is deprived, by straining and strong pressure, of as much water as possible, it may be kept in a cool place, with unaltered properties for a long time; otherwise it quickly spoils.

The distiller, who prepares spirits from grain, makes his wort, or *wash*, in the same manner as the brewer; he uses, however, with the large quantity of raw grain, the starch of which suffers conversion into sugar by the *diastase* of the malt, which is sufficient for his purpose. He does not boil his infusion with hops, but proceeds at once to the fermentation, which he pushes as far as possible by large and repeated doses of yeast. Alcohol is manufactured in many cases from potatoes. The potatoes are ground to pulp, mixed with hot water and a little malt, to furnish *diastase*, made to ferment, and then the fluid portion is distilled. The potato-spirit is contaminated by a very offensive volatile oil, again to be removed: the crude product from corn contains a substance of a similar kind. The business of the rectifier consists in removing or modifying

fyng these volatile oils, and in replacing them by others of a more agreeable character.

In making *bread*, the vinous fermentation plays an important part. the yeast added to the dough converts the small portion of sugar the meat naturally contains into alcohol and carbonic acid. The gas thus disengaged forces the tough and adhesive materials into bubbles, which are still further expanded by the heat of the oven, which at the same time dissipates the alcohol: hence the light and spongy texture of all good bread. The use of *leaven* is of great antiquity: this is merely dough in a state of incipient putrefaction. When mixed with a large quantity of fresh dough, it excites in the latter the alcoholic fermentation, in the same manner as yeast, but less perfectly: it is apt to communicate a disagreeable sour taste and odor. Sometimes carbonate of ammonium is employed to lighten the dough, being completely volatilized by the high temperature of the oven. Bread is now sometimes made by mixing a little hydrochloric acid and sodium carbonate in the dough: if proper proportions be taken and the whole thoroughly mixed, the operation appears to be very successful.

Another mode of bread-making is that invented by the late Dr. Dauglish, which consists in agitating the dough in a strong vessel with water saturated under pressure with carbonic acid gas. When the dough thus treated is subsequently released from this pressure and exposed to the air, the gas escapes in bubbles, and lightens the mass as effectually as that evolved within its substance by fermentation. The bread thus made, called "aerated bread," is of excellent quality, not being subject to the deterioration which so frequently takes place in ordinary bread, when the fermentation is allowed to go too far.

Vinous fermentation, that is to say, the conversion of sugar into alcohol and carbon dioxide, never takes place except in presence of some nitrogenous body of the albuminoid class in a state of decomposition, and it is always accompanied by the development of certain minute living organisms—fungi and infusoria—like those already mentioned as existing in yeast. So constantly indeed is this the case that many chemists and physiologists regard these organisms as the exciting cause of fermentation and putrefaction; and this view appears to be corroborated by the fact that each particular kind of fermentation takes place most readily in contact with a certain living organism, or at least with nitrogenous matter containing it: thus beer-yeast contains two species of fungus, called *Torula cerevisiæ* and *Penicillium glaucum*, the cells of which are of very different sizes, so that they may be separated by filtering an infusion of the yeast, the larger cells of the *Torula* remaining on the filter, while those of the *Penicillium*, which are much smaller, pass through with the liquid. Now, it is found that the residue on the filter brings a solution of sugar into the state of vinous fermentation, whereas the filtered liquid induces lactic fermentation, but whether this effect is due to the fungi themselves, or to the peculiar state of the albuminous matter in which they occur, is a question not yet decided. The investigation is attended with peculiar difficulties, arising chiefly from the universal diffusion of the germs of these minute organisms, which are present not only in all decaying albuminous matter, and on the skins of fruits, leaves, and other parts of plants, but are likewise diffused through the air, so that in experiments made for the purpose of ascertaining whether fermentation can take place without them, it is extremely difficult to ensure their complete exclusion from the substance under examination.*

* See the article "Fermentation," in Watts's Dictionary of Chemistry, vol. ii. p. 623.

ETHYLIC ETHERS.

Ethyl Chloride, or Chlorethane, C_2H_5Cl , or H_3C-CH_2Cl , often called *Hydrochloric ether*.—To prepare this compound, rectified spirit of wine is saturated with dry hydrochloric acid gas, and the product distilled at a very gentle heat; or a mixture of 3 parts oil of vitriol and 2 parts of alcohol is poured upon 4 parts of dry common salt in a retort, and heat applied; in either case the vapor of the hydrochloric ether should be conducted through a little tepid water in a wash-bottle, and thence into a small receiver surrounded by ice and salt. It is purified from adhering water by contact with a few fragments of fused calcium chloride.

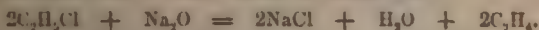
Ethyl chloride is a thin, colorless, and excessively volatile liquid, of a penetrating, aromatic, and somewhat alliaceous odor. At the freezing point of water, its sp. gr. is 0.921, and it boils at $12.5^{\circ}C.$ ($54.5^{\circ}F.$). It is soluble in 10 parts of water, is but incompletely decomposed by solution of silver nitrate when the two are heated together in a sealed tube, but is quickly resolved into potassium chloride and ethyl alcohol by a hot aqueous solution of caustic potash:



With alcoholic potash, on the other hand, or potassium ethylate, it yields ethyl oxide, or common ether:



Heated with soda-lime, it yields ethene or olefant gas:



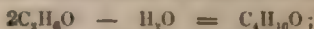
When vapor of ethyl chloride is mixed with chlorine gas in a vessel exposed, first to diffused daylight, and afterwards to direct sunshine, hydrochloric acid is formed, and the chlorine displaces one atom of hydrogen in the ethyl chloride, producing monochlorinated ethyl chloride, ethene chloride or dichlorethane, $C_2H_4Cl_2$ (p. 517). By the prolonged action of chlorine in excess, the compounds $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5 , and C_2Cl_6 , are produced (pp. 521, 522).

Ethyl Bromide, or Bromethane, C_2H_5Br , also called *Hydrobromic ether*, is prepared by distilling a mixture of 8 parts bromine, 1 part phosphorus, and 30 parts alcohol. It is a very volatile liquid, heavier than water, having a penetrating taste and odor, boiling at $41^{\circ}C.$ ($105.6^{\circ}F.$).

Ethyl Iodide, or Iodethane, C_2H_5I , also called *Hydroiodic ether*, may be conveniently prepared with 5 parts of phosphorus, 70 parts of alcohol (of 0.84 sp. gr.), and 100 parts of iodine. The phosphorus is introduced into a tubulated retort, covered with part of the alcohol, and heated to fusion. The rest of the alcohol is poured upon the iodine, and the solution thus obtained is allowed to flow gradually through a tap-funnel into the retort. The brown liquid is at once decolorized, and ethyl iodide distills over, which is condensed by a good cooling apparatus. The distillate, consisting of alcohol and ethyl iodide, is again poured on the residuary iodine, which is thus rapidly dissolved, introduced into the retort, and ultimately entirely converted into ethyl iodide. The latter is washed with water to remove adhering alcohol, separated from this water by a tap-funnel, digested with calcium chloride, and rectified in the water-bath. Ethyl iodide may also be formed by heating in a sealed glass vessel a mix-

ture of hydriodic acid and olefant gas. It is a colorless liquid, of penetrating ethereal odor, having a density of 1.92, and boiling at 72°C . (161°F). It becomes red by exposure to light, from the commencement of composition. This substance has become highly important as a source of ethyl, and from its remarkable deportment with ammonia, which will be discussed in the Section on Amines.

Ethyl Oxide, or Ethylic ether, $\text{C}_4\text{H}_{10}\text{O} = \text{C}_2\text{H}_5\text{O.C}_2\text{H}_5 = (\text{C}_2\text{H}_5)_2\text{O}$. This compound, also called *common ether*, or simply *ether*, contains the elements of 2 molecules of alcohol minus 1 molecule of water:—

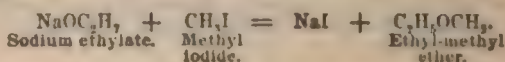


and it is in fact produced by the action of various dehydrating agents, as zinc chloride, phosphoric oxide, and strong sulphuric acid, upon alcohol. The process does not appear, however, to be one of direct dehydration; least in the case of sulphuric acid; for when that acid is heated with alcohol to a certain temperature it does not become weaker by taking water from the alcohol, but ether and water distil over together, and the sulphuric acid remains in its original state, ready to act in the same manner on a fresh portion of alcohol. The reaction is in fact one of substitution; the ultimate result being the conversion of alcohol, $\text{C}_2\text{H}_5(\text{OH})$, into ethyl ether, $\text{C}_2\text{H}_5(\text{OC}_2\text{H}_5)$, by the substitution of ethyl for hydrogen. The manner in which this takes place will be better understood when another mode of the formation of ether has been explained.

When a solution of sodium ethylate, NaOC_2H_5 , in anhydrous alcohol, obtained by dissolving sodium to saturation in that liquid, is mixed with ethyl iodide, double decomposition takes place, resulting in the formation of sodium iodide and ethyl oxide:—

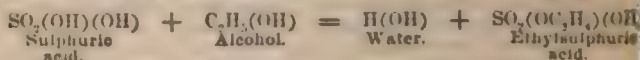


The result would be the same if chloride or bromide of ethyl were substituted for the iodide: moreover, when methyl iodide is added, instead of the ethyl iodide, an oxygen-ether is formed containing both ethyl and methyl:—

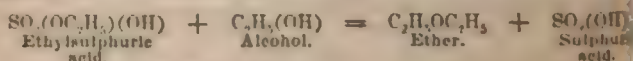


In each case the reaction consists in an interchange between the sodium and the alcohol-radicle.

Now, when alcohol is heated with strong sulphuric acid, the first result is the formation of ethylsulphuric acid, $\text{SO}_2(\text{OC}_2\text{H}_5)\text{OH}$, by substitution of ethyl for hydrogen in the acid:—



and when the ethylsulphuric acid thus formed is brought in contact with a fresh portion of alcohol, the reverse substitution takes place, resulting in the formation of ethyl oxide and sulphuric acid:—



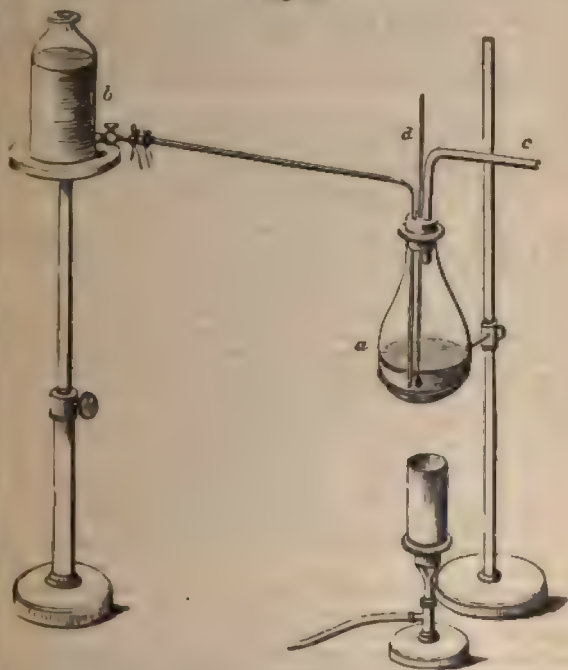
The sulphuric acid is thus reproduced in its original state, and if the quantity of alcohol be kept up, and the temperature maintained within certain limits,

the same series of actions is continually repeated, and ether and acid distil over together.

The most favorable temperature for etherification is between 127° and 154° C. (260° and 310° F.); below 127° very little ether is produced, and above 154° a different reaction takes place, resulting in the formation of ethyl gas. The maintenance of the temperature within the ether-producing limits is best effected by boiling the mixture of sulphuric acid and alcohol in a flask into which a further quantity of alcohol is supplied in a continuous and regulated stream. This is called the *continuous ether pro-*

cess. A wide-necked flask *a* (fig. 173), is fitted with a sound cork perforated by three apertures, one of which is destined to receive a thermometer with graduation on the stem; a second, the vertical portion of a long, narrow tube, terminating in an orifice of about $\frac{1}{10}$ of an inch in diameter;

Fig. 173.



the third, a wide bent tube, *c*, connected with the condenser, to carry the volatilized products. A mixture is made of 8 parts by weight of concentrated sulphuric acid, and 5 parts of rectified spirit of wine, of about 0.8 sp. gr. This is introduced into the flask, and heated by a lamp. The liquid soon boils, and the thermometer very shortly indicates a temperature of 140° C. (284° F.). When this happens, alcohol of the above density is suffered slowly to enter by the narrow tube, which is put into communication with a reservoir, *b*, of that liquid, consisting of a large

bottle perforated by a hole near the bottom, and furnished with a small brass stopcock fitted by a cork: the stopcock is secured to the end of the long tube by a caoutchouc connector. As the tube passes nearly to the bottom of the flask, the alcohol gets thoroughly mixed with the acid liquid, the pressure of the fluid column being sufficient to insure the regularity of the flow; the quantity is easily adjusted by the aid of the stopcock. For condensation a Liebig's condenser may be used, supplied with ice water.

The degree of heat, and the supply of alcohol, must be so adjusted that the thermometer may remain at 140° , or as near that temperature as possible, while the contents of the flask are maintained in a state of *capricious violent ebullition*—a point of essential importance. Ether and water distil over together, and collect in the receiver, forming two distinct strata. The mixture slowly blackens, from some slight secondary action of the acid upon the spirit, or upon the impurities in the latter, but retains, after many hours' ebullition, its etherifying powers unimpaired. The acid, however, slowly volatilizes, partly in the state of *oil of wine*, and the quantity of liquid in the flask is found, after the lapse of a considerable interval, sensibly diminished. This loss of acid constitutes the only hindrance to the duration of the process, which might otherwise be continued indefinitely.

On the large scale, the flask may be replaced by a vessel of lead, the tubes being also of the same metal: the stem of the thermometer may be made to pass air-tight through the cover, and heat may perhaps be advantageously applied by high-pressure steam, or hot oil, circulating in a spiral tube of metal immersed in the mixture of acid and spirit.

The crude ether is to be separated from the water on which it floats, agitated with a little solution of caustic potash, and redistilled by the use of warm water. The aqueous portion, treated with an alkaline solution, and distilled, yields alcohol containing a little ether. Sometimes the spontaneous separation before mentioned does not occur, from the accidental presence of a larger quantity than usual of undecomposed alcohol: the addition of a little water, however, always suffices to determine it.

Pure ethylic ether is a colorless, transparent, fragrant liquid, very dense and mobile. Its specific gravity at 15.5° C. (59.9° F.) is about 0.726; it boils at 35.6° C. (96° F.) under the pressure of the atmosphere, and bears without freezing the severest cold. When dropped on the hand it occasions a sharp sensation of cold, from its rapid volatilization. Ether is very combustible, and burns with a white flame, generating water and carbon dioxide. Although the substance itself is one of the lightest liquids, its vapor is very heavy, having a density of 2.586 (referred to air). Mixed with oxygen gas, and fired by the electric spark, or otherwise, it explodes with the utmost violence. Preserved in an imperfectly stopped vessel, ether absorbs oxygen, and becomes acid from the production of acetic acid: this attraction for oxygen is increased by elevation of temperature. It is decomposed by transmission through a red-hot tube into ethene, methane, aldehyde, and acetylene, and two substances yet to be described.

Ether is miscible with alcohol in all proportions, but not with water: it dissolves to a small extent in that liquid, 10 parts of water taking up about 1 part of ether. It may be separated from alcohol, provided the quantity of the latter is not excessive, by addition of water, and in the same manner samples of commercial ether may be conveniently examined. Ether dissolves only a few fatty substances generally, and phosphorus to a small extent, also a few saline compounds and some organic principles, but its powers in this respect are much more limited than those of alcohol and water.

Anhydrous ether, subject to the action of chlorine, yields the three eth-

stitution-products, $C_4H_5Cl_2O$, $C_4H_5Cl_3O$, and C_4Cl_5O , the first two of which are liquids, while the third, produced by the prolonged action of chlorine on ether in sunshine, is a crystalline solid. The second chlorine compound is converted by hydrogen sulphide into the two crystalline compounds $C_4H_5Cl_2SO$ and $C_4H_5Cl_3SO$.

Ethyl-methyl oxide, Ethyl-methyl ether, Ethyl methylate, or Methyl ethylate, $C_4H_{10}O = C_2H_5OCH_3$, is produced, as already mentioned, by the action of methyl iodide on potassium ethylate, or of ethyl iodide on potassium methylate. It is a very inflammable liquid, boiling at $11^\circ C.$ ($51.8^\circ F.$).

Ethyl Nitrate, $C_2H_5NO_3$, or $C_2H_5ONO_2$.—*Nitric ether*.—When nitric acid is heated with alcohol alone, part of the alcohol is oxidized, and the nitric acid is reduced to nitrous acid, which, with the remainder of the alcohol, forms ethyl nitrite, $C_2H_5NO_2$, together with other products; but by adding area to the liquid, which decomposes the nitrous acid as fast as it is formed, this action may be prevented, and the alcohol and nitric acid then form ethyl nitrate. The experiment is most safely conducted on a small scale, and the distillation must be stopped when seven-eighths of the whole have passed over; a little water added to the distilled product separates the nitric acid. Nitric ether boils at 85° or $86^\circ C.$ (185° – $186.8^\circ F.$), and has a density of 1.112 at $15^\circ C.$ ($59^\circ F.$); it is insoluble in water, has an agreeable sweet taste and odor, and is not decomposed by an aqueous solution of caustic potash, although that substance dissolved in alcohol attacks it even in the cold, with production of potassium nitrate. Its vapor is apt to explode when strongly heated.

Ethyl Nitrite, $C_2H_5NO_2 = C_2H_5-O-NO$.—*Nitrous ether*.—This compound, isomeric with nitro-ethane, $C_2H_5-NO_2$, can be obtained pure only by the direct action of the acid itself upon alcohol. One part of starch and 10 parts of nitric acid are gently heated in a capacious retort or flask, and the vapor of nitrous acid thereby evolved is conducted into alcohol mixed with half its weight of water, contained in a two-necked bottle, which is to be plunged into cold water, and connected with a good condensing arrangement. Rise of temperature must be carefully avoided. The product of this operation is a pale-yellow volatile liquid, having an exceedingly agreeable odor of apples: it boils at $16.4^\circ C.$ ($61.5^\circ F.$), and has a density of 0.947 at $15^\circ C.$ ($59^\circ F.$). It is decomposed by potash, without darkening, into potassium nitrite and alcohol.

The *sweet spirits of nitre* of pharmacy, prepared by distilling three pounds of alcohol with four ounces of nitric acid, is a solution of nitrous ether, aldehyde, and several other substances, in spirit of wine.

Ethyl Sulphates.—There are two of these ethers, analogous to the methyl sulphates.

Acid Ethyl Sulphate, Ethylsulphuric acid, or Sulphovinic acid, $C_4H_8SO_4 = C_2H_5O.SO_3H = SO_3(OC_2H_5)(OH) = SO_3(C_2H_5)H$, which has the composition of sulphuric acid, SO_3H_2 , with half the hydrogen replaced by ethyl, is formed by the action of sulphuric acid upon alcohol. To prepare it, strong rectified spirit of wine is mixed with twice its weight of concentrated sulphuric acid: the mixture is heated to its boiling point, and then left to cool. When cold it is diluted with a large quantity of water, and neutralized with chalk, whereby much calcium sulphate is produced. The mass is placed upon a cloth filter, drained, and pressed; and the clear solution is evaporated to a small bulk by the heat of a water-bath, filtered from a little sulphate, and left to crystallize: the product is calcium ethylsulphate,

in beautiful, colorless, transparent crystals, containing $\text{Ca}(\text{C}_2\text{H}_5)_2(\text{SO}_3) \cdot 2\text{H}_2\text{O}$. They dissolve in an equal weight of cold water, and effervesce in a dry atmosphere.

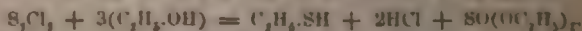
Barium Ethylsulphate, $\text{Ba}(\text{C}_2\text{H}_5)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, equally soluble, and still more beautiful, may be produced by substituting, in the above process, barium carbonate for chalk. From this salt the acid may be produced by exactly precipitating the base with dilute sulphuric acid, and evaporating the filtered solution in a vacuum at the temperature of the air. It forms a sour, syrupy liquid, in which sulphuric acid cannot be recognized by the ordinary reagents, and is very easily decomposed by heat, and even by long exposure in the vacuum of the air-pump. All the ethylsulphates are soluble; the solutions are decomposed by boiling. The *lead-salt* resembles the barium-compound. The *potassium salt*, $\text{K}(\text{C}_2\text{H}_5)_2\text{SO}_4$,—easily made by decomposing calcium ethylsulphate with potassium carbonate—is anhydrous, permanent in the air, very soluble, and crystallizes well.

Potassium ethylsulphate distilled with strong sulphuric acid, yields ethyl oxide with dilute sulphuric acid, alcohol; and with strong acetic acid, ethyl acetate.

Isethionic acid, isomeric with ethylsulphuric acid, will be described amongst ethenic ethers.

Neutral Ethyl sulphate $(\text{C}_2\text{H}_5)_2\text{SO}_4$, or $\text{SO}_4(\text{OC}_2\text{H}_5)_2$, is formed by passing the vapor of sulphuric oxide into perfectly anhydrous ether. A colorless liquid is produced, which, when shaken with 4 volumes of water and 1 volume of ether, separates into two layers, the lower containing ethylsulphuric acid and various other compounds, while the upper layer consists of an ethereal solution of neutral ethyl sulphate. At a gentle heat the ether is volatilized, and the ethyl sulphate remains as a colorless liquid. It cannot be distilled without decomposition.

Ethyl Sulphites.—The *symmetric neutral sulphite*, $\text{SO} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$, is formed by the action of thionyl chloride, SOCl_2 , or of sulphur dichloride, S_2Cl_2 , on absolute alcohol:—



The mercaptan, likewise formed in the last reaction, suffers further decomposition.

Ethyl sulphite is a limpid, strong-smelling liquid, having a specific gravity of 1.085 at 0°, boiling at 161° C. (321.8° F.), decomposed by water into alcohol and sulphurous acid. With *phosphorus pentachloride* it forms the chloride, $\text{SO} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{Cl} \end{smallmatrix}$ (isomeric with ethylsulphonic chloride), which boils at 122° C. (251.6° F.), and is decomposed by water into alcohol, hydrochloric acid and sulphurous acid.

When ethyl sulphite is mixed with an equivalent quantity of potassium hydroxide in dilute solution, crystalline scales are formed, consisting of the salt, $\text{SO} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OK} \end{smallmatrix}$, which may be regarded as the potassium-salt of ethylsulphurous acid, isomeric with ethylsulphonic acid. The aqueous solution of this salt easily splits up into potassium sulphite and ethyl alcohol.

Ethylsulphonic acid, $\text{C}_2\text{H}_5\text{SO}_3\text{OH}$, formed by the action of *nitric fuming* on potassium or sodium sulphite (p. 564), is a thick crystalline

which is oxidized by nitric acid to ethylsulphuric acid, $\text{SO}_4(\text{C}_2\text{H}_5)_2\text{H}$. The ethyl salt, $(\text{C}_2\text{H}_5)_2\text{SO}_4\text{Pb}$, crystallizes in easily soluble laminae. The ethyl salt, $\text{C}_2\text{H}_5\text{SO}_4\text{OC}_2\text{H}_5$, likewise obtained by heating silver sulphite and iodide, is a liquid having a specific gravity of 1.17 at 0° , and 20°C . (406.4 F.).

Ethylsulphide, $\text{C}_2\text{H}_5\text{SO}_2\text{Cl}$, is a liquid boiling at 173°C . (343.4°F .).

Ethylsulphonic acid, $\text{C}_2\text{H}_5\text{ClSO}_2\text{OH}$, is produced by the action of phosphatichloride on isethionic acid, $\text{C}_2\text{H}_4(\text{OH})\text{SO}_2\text{H}$.

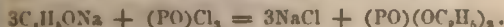
Sulphinic Acid, $\text{C}_2\text{H}_5\text{SO.OH}$.—The zinc salt, $(\text{C}_2\text{H}_5\text{SO})_2\text{Zn}$, by the action of sulphur dioxide on zinc ethide (p. 555), crystallizes in laminae. By oxidation with nitric acid, the acid is converted into ethylsulphonic acid.

Phosphates.—Three ethyl orthophosphates have been obtained, and one neutral, analogous in composition to the sodium phosphate and a neutral pyrophosphate.

Ethyl Phosphate, or *Ethylphosphoric acid*, $(\text{C}_2\text{H}_5)_2\text{H}_2\text{PO}_4$, or $(\text{PO})'''(\text{OC}_2\text{H}_5)_2$, is called *Phosphoric acid*.—This acid is dibasic. Its barium salt is obtained by heating to 82°C . (179.6°F .) a mixture of equal weights of alcohol and syrupy phosphoric acid, diluting this mixture, after a few hours, with water, and neutralizing with barium carbonate. The ethylphosphate, separated by filtration from the insoluble phosphates, evaporated at a moderate temperature. The salt crystallizes in hexagonal plates, which have a pearly lustre, and are more soluble than in hot water; it dissolves in 15 parts of water at 20°C .

The crystals contain $(\text{C}_2\text{H}_5)_2\text{BaPO}_4 \cdot 6\text{H}_2\text{O}$. From this salt the acid can be obtained by precipitating the barium with dilute sulphuric acid, evaporating the filtered liquid in the vacuum of the air-pump; it is colorless, syrupy liquid, of intensely sour taste, sometimes exhibiting traces of crystallization. It is very soluble in water, alcohol, and easily decomposed by heat when in a concentrated state. Ethyl phosphates of calcium, silver, and lead are but slightly soluble; the alkali-metals, magnesium, and strontium, are freely soluble.

Diethyl Phosphate, or *Diethylphosphoric acid*, $(\text{C}_2\text{H}_5)_2\text{HPO}_4$, or $(\text{PO})'''(\text{OC}_2\text{H}_5)_2$, is a monobasic acid, obtained, together with the preceding, by heating of syrupy phosphoric acid upon alcohol. Its barium, silver, and lead salts are more soluble than the methyl phosphates. The calcium salt, $\text{Ca}(\text{PO}_4)_2$, and the lead salt, $(\text{C}_2\text{H}_5)_2\text{Pb}(\text{PO}_4)_2$, are anhydrous. **Triethyl Phosphate**, $(\text{C}_2\text{H}_5)_3\text{PO}_4$, or $(\text{PO})'''(\text{OC}_2\text{H}_5)_3$, is obtained in small quantity by heating the lead salt of diethylphosphoric acid to 100° ; more abundantly by the action of ethyl iodide on triargentic phosphate, or of phosphatichloride on sodium ethylate:—



It is a liquid of specific gravity 1.072 at 12°C . (53.6°F .), boiling at 141°C . (286°F .), soluble in alcohol and ether, and also in water, by which, however, it is slowly decomposed.

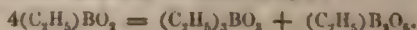
Triethyl Pyrophosphate, $(\text{C}_2\text{H}_5)_4\text{P}_2\text{O}_7$, produced by the action of ethyl argentic pyrophosphate, is a viscid liquid of specific gravity 1.17 at 20°C . (62.6°F .), decomposed by potash, with formation of potassium ethyl-phosphate.

Phosphites.—*Symmetrical Triethyl Phosphite*, $\text{P}(\text{O.C}_2\text{H}_5)_3$, formed by the action of phosphorus trichloride on ethyl alcohol, boils at 191°C .

Ethylphosphonic acid, $(\text{C}_2\text{H}_5)_2\text{PO}(\text{OH})_2$, formed by oxidation of primary ethylphosphine with nitric acid, is a solid body melting at 44°C . (111.2°F .).

gravity of 0.690, and boiling at 95° C. (203° F.).

Monethylic Borate, $C_2H_5BO_2$, is a dense inodorous liquid, having the consistence of oil of vitriol. It cannot be distilled without decomposition, being resolved at high temperatures into triethylic monethylic triborate, $C_6H_5B_3O_9$, or $C_2H_5BO_2 \cdot B_2O_3$:



The latter remains as a mass resembling gum-arabic: it attracts from the air, and becomes covered with a crust of boric acid.

Ethyl Silicates.—*Tetreethylic Silicate*, $(C_2H_5)_4SiO_4$, or $Si(C_2H_5)_4$, is produced by treating silicic chloride with a small quantity of alcohol:



It is a colorless liquid, having a rather pleasant ethereal odor, peppery taste; specific gravity 0.933 at 20° C. (68° F.). It begins to decompose between 165° and 166° C. (329° and 330.8° F.) set on fire burns with a dazzling flame, diffusing a white smoke of divided silica. It is decomposed slowly by water, quickly by acids and the fixed alkalies.

Silicic ethers containing ethyl and methyl, and ethyl and methyl, likewise been obtained.

Ethylic Thio-alcohol and Ethers.

Ethyl Hydrosulphide, Ethylic Thio-alcohol, or Methyl Ethyl Sulphide, C_2H_5SH .—This compound, the sulphur analogue of ethyl alcohol, is produced, analogously to methyl hydrosulphide (p. 562), by the action of potassium hydrosulphide on calcium ethylsulphate. A solution of potash of specific gravity 1.28 or 1.3, is saturated with sulphur dioxide, and mixed in a retort with an equal volume of solution

ed, soluble in alcohol, and separating from that liquid in distinct layers which contain $\text{Hg}(\text{SC}_2\text{H}_5)_2$. This compound is decomposed by heated hydrogen, mercuric sulphide being thrown down, and mercury reproduced. By adding solutions of lead, copper, silver, and gold in alcoholic solution of mercaptan, corresponding compounds containing these metals are formed. Caustic potash produces no effect upon mercury, but potassium displaces hydrogen, and gives rise to a crystalline compound, $\text{C}_2\text{H}_5\text{SK}$, soluble in water. Sodium acts in a similar manner.

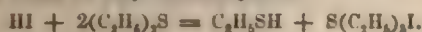
Ethyl Sulphides.—Three of these compounds have been obtained, differing in composition to the methyl sulphides, and produced by similar methods. The monosulphide, $(\text{C}_2\text{H}_5)_2\text{S}$, or $\text{C}_2\text{H}_5\text{SC}_2\text{H}_5$, is a colorless oily liquid having a very pungent alliacious odor, a specific gravity of 0.825 at 68°F ., and boiling at 91°C . (195.8°F .). It is very inflammable, burning with a blue flame. When poured into chlorine gas, it reacts; but when dry chlorine is passed into a flask containing it, not into the liquid, the vessel being kept cool and in the shade, substitution-products are formed and hydrochloric acid is copiously evolved. The product consists chiefly of dichlorethylic sulphide, $(\text{C}_2\text{H}_4\text{Cl})_2\text{S}$. The action takes place in diffused daylight, and without external cooling. Compounds $(\text{C}_2\text{H}_3\text{Cl}_2)_2\text{S}$ and $(\text{C}_2\text{HCl}_3)_2\text{S}$ are obtained, which may be separated by fractional distillation, the first boiling between 189° and $(372.2-377.6^\circ\text{F}.)$, the second between 217° and 222°C . ($422.6-429.6^\circ\text{F}.$). The action of chlorine on ethyl sulphide in sunshine yields a highly chlorinated compound, probably $(\text{C}_2\text{Cl}_5)_2\text{S}$.

The bisulphide, $(\text{C}_2\text{H}_5)_3\text{S}_2$, obtained by distilling potassium bisulphide or potassium ethylsulphate or with ethyl oxalate, is a colorless oily liquid, very inflammable, boiling at 151°C . ($303.8^\circ\text{F}.$). The trisulphide, S_3 , is a heavy oily liquid, obtained by acting in like manner on ethyl pentasulphide.

Ethylsulphurous Compounds.—When ethyl monosulphide and ethyl iodide are heated together, they unite and form sulphurous triethylide, $(\text{C}_2\text{H}_5)_3\text{S}(\text{C}_2\text{H}_5\text{I})$, or $\text{S}^{\text{iv}}(\text{C}_2\text{H}_5)_3\text{I}$, which crystallizes in needles. The same compound is formed by the action of ethyl iodide on ethyl disulphide:



or by the action of ethyl iodide on ethyl monosulphide:



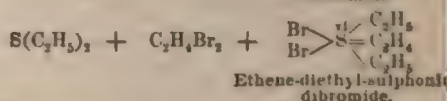
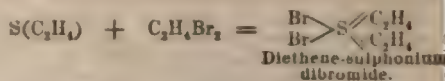
Sulphurous triethylide is insoluble in ether, slightly soluble in alcohol, and crystallizes from the solution in white deliquescent needles belonging to the monoclinic system. It unites with metallic chlorides.

Ethyl chloride and ethyl bromide unite in like manner, but less readily, with ethyl sulphide, forming the compounds $\text{S}(\text{C}_2\text{H}_5)_3\text{Cl}$ and $\text{S}(\text{C}_2\text{H}_5)_3\text{Br}$, which crystallize in needles.

By acting the iodine compound with recently precipitated silver oxide, in an alkaline solution is obtained, which dries up over oil of vitriol into a white deliquescent mass, consisting of sulphurous triethyl oxalate, $(\text{C}_2\text{H}_5)_3\text{S}(\text{OH})$. The solution of this substance dissolves in water like caustic potash, and forms similar precipitates with various metallic salts. It neutralizes acids, forming definite crystallizable salts, such as the nitrate, $(\text{C}_2\text{H}_5)_3\text{S}(\text{ONO}_2)$, the acetate, $(\text{C}_2\text{H}_5)_3\text{S}(\text{OC}_2\text{H}_5\text{O})$, etc.

The action of the sulphur in these compounds is analogous to that of

thus :—



Analogous compounds are also formed by selenium, e. g., *Tellurium iodide*, $Se(CH_3)_2I_2$.

Ethyl Telluride, Tellurio Ethide or Tellurethyl, $Te(C_2H_5)_2$ compound is obtained by distilling potassium telluride with ethylsulphate :—



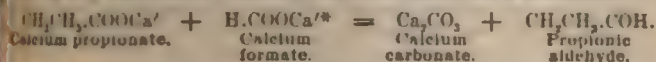
It is a heavy, oily, yellowish-red liquid, very inflammable, and most intolerable odor. It acts as a bivalent radicle, uniting with bromine, oxygen, etc., to form compounds in which the tellurium is a tetrad, e. g., $Te(C_2H_5)_4Cl_2$, $Te(C_2H_5)_4O$, etc. The *nitrate* is obtained by treating tellurethyl with nitric acid; the other salts by double decomposition; the *chloride*, for example, settles down as a heavy oil, on adding hydrochloric acid to a solution of the nitrate. The *oxide* is best prepared by treating the chloride with water and silver oxide; it dissolves in water, forming a slightly alkaline liquid.

Selenic Ethide, or Selenethyl, $Se(C_2H_5)_2$, prepared like tellurethyl, is also a fetid liquid, exactly resembling the tellurium compound in its chemical relations.

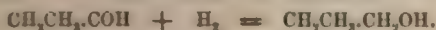
Normal Propyl Alcohol was discovered by Chancel in 1853, in the distillate of the residues left in the distillation of brandy from wine. It can be obtained synthetically from ethyl alcohol by the following series of processes:—

1. Ethyl cyanide, C_2H_5N , or CH_3CH_2CN (prepared by distilling a mixture of potassium cyanide and potassium ethylsulphate, p. 527), is converted into propionic acid, CH_3CH_2COOH , by boiling with strong caustic potash.

2. A mixture of the calcium salts of propionic and formic acids is subjected to dry distillation, whereby propionic aldehyde is obtained:—

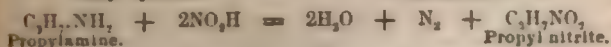
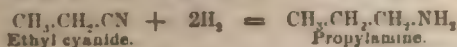


3. The propionic aldehyde, treated with water and sodium amalgam, takes up 2 atoms of hydrogen, and is converted into normal propyl alcohol:—



The series of processes just described affords a general method of building up the normal primary alcohols of the fatty group, one from the other. It has not, however, been actually carried out higher than the six-carbon hexyl alcohol.

Another method of passing from ethyl-alcohol to propyl alcohol—also generally applicable as a method of synthesis of primary alcohols—is to convert ethyl cyanide or propionitril into propylamine by the action of nascent hydrogen (water and sodium amalgam) and the propylamine, by the action of nitrous acid, into propyl nitrite, which may then be converted into the alcohol by distillation with an alkali:—



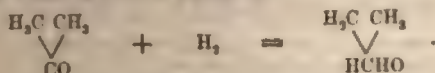
Normal propyl alcohol is an oily liquid, boiling at $96^\circ C.$ ($204.80^\circ F.$), and having a specific gravity of 0.8205 at $0^\circ C.$ By oxidation with a mixture of sulphuric acid and potassium dichromate, it is converted into propionic acid.

Normal propyl chloride, C_3H_7Cl , boils at $46.5^\circ C.$ ($115.7^\circ F.$); the bromide at $70-71^\circ C.$ ($158-159.8^\circ F.$); the iodide at $102^\circ C.$ ($215.6^\circ F.$); the oxide, $(C_3H_7)_2O$, at $85-86^\circ C.$ ($185-186.8^\circ F.$).

Pseudopropyl Alcohol, or Secondary Propyl Alcohol,

$CH_3CH_2CH_2OH$.—This alcohol is prepared:

1. From acetone, $(CO)(CH_3)_2$, by direct addition of hydrogen, evolved by the action of water on sodium amalgam:



This mode of synthesis affords direct proof of the constitution of pseudopropyl alcohol, the addition of the two hydrogen-atoms being tantamount to the replacement of the bivalent radicle oxygen by the two monad radicles, hydrogen and hydroxyl.

* For the sake of simplicity, the equivalent (20) of calcium is used in this equation, instead of the atomic weight.

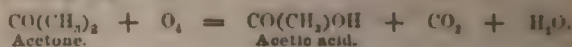
2. Pseudopropyl iodide is prepared by the action of iodine and phosphorus on *glycerin*; this iodide is easily converted into the oxalate or acetate by treatment with silver oxalate or acetate; and from either of these ethers the alcohol may be obtained by distillation with potash or soda.

Pseudopropyl alcohol is a colorless, not very mobile liquid, having a peculiar odor, a specific gravity of 0.791 at 15° C. (59° F.), boiling at 81° C. (181.4–183.2° F.) under a barometric pressure of 739 millimetres, not freezing at –20° C. (4° F.). It does not act on polarized light. It is very difficult to dry, as it mixes with water in all proportions, and forms with it three definite and very stable hydrates, viz., $3C_3H_7O \cdot 2H_2O$, boiling at 78°–80° C. (172.4–176° F.); $2C_3H_7O \cdot H_2O$, boiling at 80° C. (176° F.); and $3C_3H_7O \cdot H_2O$, boiling at 81° C. (177.8° F.). The second of these hydrates exhibits a very close resemblance to ethyl alcohol, has the same percentage composition, boils at nearly the same temperature, and likewise yields acetic acid by oxidation (see below), moreover it retains its water of hydration so obstinately, that it does not even change the white color of anhydrous cupric sulphate to blue. The readiest mode of distinguishing between this hydrate and ethyl alcohol is to submit them to the action of iodine and phosphorus, whereby the former is converted into pseudopropyl iodide, the latter into ethyl iodide.

The characteristic property of pseudopropyl alcohol is that it yields acetone by oxidation with dilute chromic acid, this transformation being the reverse of that by which it is produced:



On pushing the oxidation further, the acetone breaks up into acetic acid and carbon dioxide, and water:

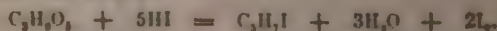


The evolution of carbon dioxide in this reaction affords a further distinction between hydrated pseudopropyl alcohol and ethyl alcohol.

The formation of a ketone by oxidation is, as already observed, the essential characteristic of a secondary alcohol, and is an immediate consequence of its structure (p. 558).

Pseudopropyl alcohol, heated with acetic acid, or with potassium acetate and sulphuric acid, is converted into *pseudopropyl acetate*, $CH(CH_3)_2 \cdot C_2H_3O_2$.

PSEUDOPROPYL IODIDE, $CH(CH_3)_2I$, is most conveniently prepared by the action of hydroiodic acid, concentrated and in large excess, on glycerol (propenyl alcohol) $C_3H_7O_2$:



The iodine, as fast as it is set free by the reaction, may be reconverted into hydroiodic acid by means of phosphorus, and will then be ready to act upon another portion of glycerol. The iodide may also be produced by the action of hydroiodic acid on pseudopropyl alcohol, allyl iodide, C_3H_7I , propene, or propene alcohol.

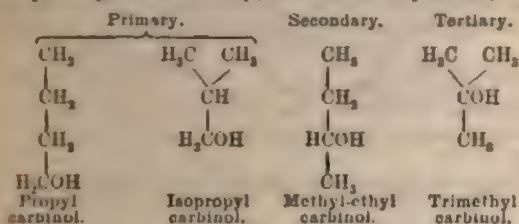
Pseudopropyl iodide is an oil boiling at 80°–90° C. (176°–194° F.), and having a specific gravity of 1.70. With sodium in presence of ether it yields propene, propane, and di-isopropyl, C_6H_{14} (p. 500). Bromine expels the iodine, and forms pseudopropyl bromide.

By treatment with zinc and hydrochloric acid, which evolves hydrogen

pseudopropyl iodide is converted into propane: $C_3H_7I + H_2 = HI + C_3H_8$; the propane, exposed to the action of chlorine in diffused daylight, is partly converted into normal propyl chloride; this compound, heated with potassium acetate and strong acetic acid, yields normal propyl acetate; and the latter, heated with potash-lye in sealed tubes, yields normal propyl alcohol. This series of reactions affords a general method of converting a secondary alcohol into the corresponding normal primary alcohol.

TETRYL OR BUTYL ALCOHOLS AND ETHERS.

Theory indicates the existence of four alcohols included in the formula $C_4H_{10}O$, two primary, one secondary, and one tertiary; thus,



Propyl Carbinol, or Normal Butyl Alcohol, $C \begin{cases} CH_2CH_2CH_3 \\ H_2 \\ OH \end{cases}$.—This

alcohol is obtained from butyl chloride, C_4H_9Cl (produced by the action of chlorine on butane or diethyl, C_4H_{10}), by heating that chloride with potassium acetate and strong acetic acid, whereby it is converted into butyl acetate, and treating that compound with barium hydrate. It may also be prepared from normal propyl alcohol, in the same manner as the latter is obtained from ethyl alcohol, viz., by successive conversion into propyl cyanide or butyronitril, C_4H_9N or $CH_3CH_2CH_2CH_2CN$, normal butyric acid, $CH_3CH_2CH_2COOH$, butyric aldehyde, $CH_3CH_2CH_2COH$ (prepared by heating a mixture of the calcium salts of butyric and formic acids), and finally into the alcohol, $CH_3CH_2CH_2CH_2OH$, by the action of nascent hydrogen on the aldehyde, or, lastly, by converting the butyronitril into butylamine, $C_4H_{11}N$, the latter into butyl nitrite by the action of nitrous acid, and distilling the nitrite with an alkali.

Normal butyl alcohol boils at $115^\circ C.$ ($239^\circ F.$), smells like isobutyl alcohol, is much lighter than water, slightly soluble therein; with iodine and phosphorus it yields normal butyl iodide, boiling at $127^\circ C.$ ($260.6^\circ F.$). Oxidation with dilute chromic acid converts it into normal butyric acid $CH_3CH_2CH_2COOH$.

Isopropyl Carbinol, or Isobutyl Alcohol, $C \begin{cases} CH(CH_3)_2 \\ H_2 \\ OH \end{cases}$.—This va-

riety of primary butyl-alcohol was found by Wurtz in the fusel-oil obtained by fermenting the molasses of beet-root sugar. To separate it, this oil is submitted to fractional distillation, and the liquid boiling between $108^\circ C.$ ($226.4^\circ F.$) and $118^\circ C.$ ($244.4^\circ F.$) is repeatedly rectified over potassium hydroxide, till it boils constantly at $110^\circ C.$ ($230^\circ F.$).

Pure isobutyl alcohol is a colorless liquid, having an odor somewhat like

that of amyl alcohol, but less pungent, and more vinous: specific gravity = 0.8032 at 18.5° C. (65.3° F.). It dissolves in 10½ times its weight of water, and is separated therefrom, as an oil, by calcium chloride, sodium chloride, and other soluble salts. By oxidation it is converted into isobutyric acid, $\text{CH}(\text{CH}_3)_2\text{COOH}$.

Isobutyl alcohol is acted upon by acids and other chemical reagents much in the same manner as common alcohol. With strong sulphuric acid it yields isobutyl-sulphuric acid, $(\text{C}_4\text{H}_9)\text{HSO}_4$, if the mixture is kept cool, but on heating the liquid, isobutene, $\begin{matrix} \text{H}_3\text{C} \\ \text{H}_2\text{C} \end{matrix} > \text{C}-\text{CH}_3$, is given off mixed with sulphurous oxide and carbon dioxide. Heated with hydrochloric acid in a sealed tube, or treated with phosphorus pentachloride or oxychloride, it is converted into isobutyl chloride or chloro-isobutane $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{Cl}$, an ethereal liquid, having a pungent odor, and boiling at 70° C. (158° F.). Isobutyl bromide, $\text{C}_4\text{H}_9\text{Br}$, obtained in the same manner, boils at 89° C. (192.2° F.), the iodide, $\text{C}_4\text{H}_9\text{I}$, at 121° C. (249.8° F.). The iodide is decomposed by potassium or sodium, yielding iso-o-

tane or iso-dibutyl, $\begin{matrix} (\text{CH}_3)_2\text{CH}-\text{CH}_3 \\ (\text{CH}_3)_2\text{CH}-\text{CH}_2 \end{matrix}$, a limpid liquid, lighter than water, and boiling at 105° C. (221° F.). The same hydrocarbon is obtained by the electrolysis of ordinary valeric acid, $\text{C}_5\text{H}_{10}\text{O}_2$.

Methyl-ethyl Carbinol, or Secondary Butyl Alcohol, $\text{C} \begin{cases} \text{CH}_3 \\ \text{C}_2\text{H}_5 \\ \text{H} \\ \text{OH} \end{cases}$

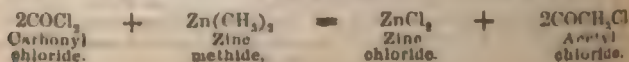
This alcohol is obtained from erythrite, a saccharine substance having the composition of a tetratomic alcohol, $\text{C}_4\text{H}_{10}\text{O}_4$, or $\text{C}_4\text{H}_8(\text{OH})_4$. The erythrite distilled with fuming hydriodic acid, yields methyl-ethyl-iodomethane or secondary butyl iodide, $\text{C}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{HI}$, and this liquid, treated with moist silver oxide is converted into methyl-ethyl carbinol:

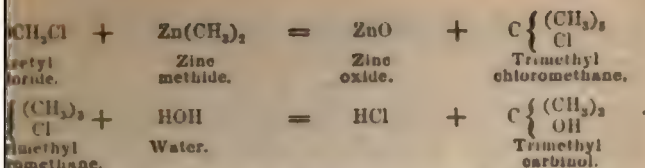


Methyl-ethyl carbinol is a colorless oily liquid, having a strong odor and burning taste, a specific gravity of 0.85 at 0°, and boiling at 95° C. (203° F.) (about 20° C. (36° F.) lower than the normal primary alcohol). When heated at 250° C. (482° F.), it is for the most part resolved into water and butene: $\text{C}_4\text{H}_{10}\text{O} = \text{H}_2\text{O} + \text{C}_4\text{H}_8$.

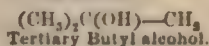
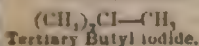
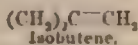
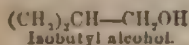
Methyl-ethyl-iodomethane, or Secondary Butyl iodide, prepared as above, by the action of strong hydriodic acid on the alcohol, is a liquid having a pleasant ethereal odor, a specific gravity of 1.632 at 0°, 1.600 at 20° C. (68° F.), and 1.584 at 30° C. (86° F.). It boils at 118° C. (244.4° F.). Bromine decomposes it, expelling the iodine and forming butene dibromide, $\text{C}_4\text{H}_8\text{Br}_2$. When distilled with alcoholic potash, it gives off butene. This tendency to give off the corresponding olefine is characteristic of all the secondary alcohols and ethers, as will be further noticed in connection with the five-carbon compounds.

Trimethyl Carbinol, or Tertiary Butyl Alcohol, $\text{C} \begin{cases} (\text{CH}_3)_3 \\ \text{OH} \end{cases}$, is produced by treating zinc methide with carbonyl chloride (phosgene gas) or acetyl chloride, and submitting the product to the action of water.





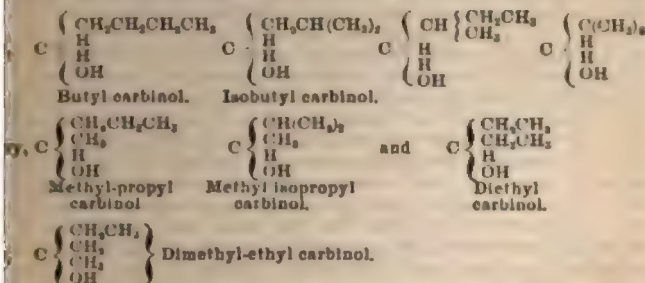
may also be formed from the primary isoalcohol by the following processes: (1) The alcohol treated with sulphuric acid, or other acting agent, yields isobutene, C_4H_8 .—(2) This olefine, treated with hydriodic acid, yields tertiary butyl iodide, the iodine attached to the carbon atom which is not in direct combination with hydrogen.—(3) The iodide treated with silver oxide is converted into the alcohol. The series of transformations is represented by the following formulæ:—



Methyl carbinol, when perfectly anhydrous, crystallizes in rhombic prisms, melting at 25.5°C . (77.9°F). In the liquid state it has a specific gravity of 0.7788 at 30°C . (86°F), and boils at 82.5°C . (180.5°F). It mixes with water in all proportions, and likewise forms a hydrate, $2\text{C}_4\text{H}_{10}\text{O} \cdot \text{H}_2\text{O}$, which crystallizes in a freezing mixture, and without decomposition at 80°C . (176°F). By oxidation with chromic acid, trimethyl carbinol is resolved into acetic acid and acetone, and with a small quantity of isobutyric acid.

PENTYL ALCOHOLS AND ETHERS.

The formula $\text{C}_5\text{H}_{12}\text{O}$ may include eight different alcohols: four primary, two secondary, and one tertiary, viz.:—



These are known, viz., the first, second, fifth, sixth, seventh, and

Normal Primary Pentyl Alcohol.

Normal Primary Pentyl Alcohol, $\text{C}_5\text{H}_{12}\text{O}$, is prepared from normal butyl alcohol in the same manner

as the latter from normal propyl alcohol, viz., by successive conversion into butyl cyanide, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$, normal valeric acid, $\text{CH}_3(\text{CH}_2)_4\text{COOH}$, valeric aldehyde, $\text{CH}_3(\text{CH}_2)_3\text{CHO}$, and the alcohol, $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$. It is a liquid boiling at 135°C . (275°F .), $d_{44} = 0.823$, higher than isopentyl alcohol. The chloride, bromide, iodide, and acetate obtained from it boil at higher temperatures than the corresponding isopentyl compounds. By oxidation it yields normal valeric acid.

Isobutyl Carbinol, Isopentyl Alcohol, or Amyl Alcohol,

$\text{CH}_3\left\{\begin{array}{l} \text{C}_4\text{H}_9\text{OH} \\ (\text{CH}_3)_2 \end{array}\right.$. — This is the ordinary amyl alcohol produced by fermentation.

In the manufacture of brandy from corn, potatoes, or the musts of grapes, the ethyl alcohol is found to be accompanied by an acrid oil liquid called *fusel-oil*, which is very difficult to separate completely from the ethyl alcohol. It passes over, however, in considerable quantity towards the end of the distillation, and may be collected apart, washed by agitation with several successive portions of water to free it from ethyl alcohol, and re-distilled. The liquid thus obtained consists chiefly of amyl alcohol, sometimes mixed with propyl, butyl, and other alcohols. The amyl alcohol may be obtained pure by fractional distillation, the portion which passes over between 128° and 132°C . (262.4° and 269.6°F .) being collected apart. Potato fusel-oil consists almost wholly of ethyl and amyl alcohols, the latter constituting the greater quantity.

Amyl alcohol is an oily, colorless, mobile liquid, having a peculiar odor and a burning acrid taste. Its vapor when inhaled produces coughing and oppression of the chest. It has a specific gravity of 0.825 at 65° , and boils at 130°C . (266°F .). When dropped on paper it forms a greasy stain, which, however, disappears after a while. It is not perceptibly soluble in water, but floats on the surface of that liquid like an oil. It dissolves in common alcohol, ether, and various essential oils dissolve it readily.

Amyl alcohol usually exerts a rotatory action on polarized light by the rotatory power varies considerably in different samples. Pasteur, indeed, has shown that ordinary amyl alcohol is a mixture of two isomeric alcohols, having the same vapor-density, but differing in their optical properties, one of them turning the plane of polarization to the right, whereas the other is optically inactive. They are separated by converting the crude amyl alcohol into amylsulphuric acid, saturating with barium carbonate, and crystallizing the barium amylsulphate thus formed. The salt obtained from the active amyl alcohol is $2\frac{1}{2}$ times more soluble than that obtained from the inactive alcohol, and consequently the latter crystallizes out first, and by precipitating the barium from the solution of either salt with sulphuric acid, and distilling the amylsulphuric acid thus separated with water, the corresponding amyl alcohol is obtained. The difference of optical character between the two alcohols—which is traceable through many of their derivatives—has not been satisfactorily explained; but it perhaps depends upon the arrangement of the molecules, rather than upon that of the atoms within the molecules. On the other hand, it is possible that the active and inactive alcohols may contain different radicals, as indicated by the second, third, and fourth formulae of primary amyl alcohols above given.

Vapor of amyl alcohol passed through a red-hot tube, yields a mixture of ethene, propene, butene, and isopentene or amylenes.

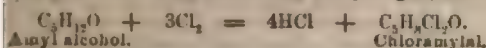
Amyl alcohol takes fire easily and burns with a blue flame. When exposed to the air in contact with platinum black, or treated with a mixture of potassium chromate and dilute sulphuric acid, it is oxidized to isovaleric acid, $\text{CH}_3\text{CH}(\text{CH}_3)_2\text{COOH}$.

Amyl alcohol, heated to 220°C . (428°F .) with a mixture of potassium

al lime, is converted into potassium valerate, with evolution of

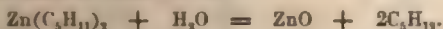


and sodium dissolve in amyl alcohol as in ethyl alcohol, yielding compounds, $C_5H_{11}KO$, and $C_5H_{11}NaO$, which, when treated with H_2SO_4 , yield amyl oxide or amyl ether, $(C_5H_{11})_2O$, and with HCl , ethyl-amyl oxide, $(C_2H_5)(C_5H_{11})O$. It acts upon amyl alcohol as upon ethyl alcohol (p. 564), except that it finally removes only four atoms of hydrogen, instead of five:



Amyl alcohol is acted upon by acids, like common alcohol, yielding when mixed with strong sulphuric acid, it is converted into amyl-sulphate, $(C_5H_{11})HSO_4$; and, on distilling the mixture, amyl oxide, $(C_5H_{11})_2O$, passes over, together with amylene, and several other hydro-

AMYL CHLORIDE, or AMYL CHLORIDE, $C_5H_{11}Cl$, or $HC\{C_5H_{11}\}$, is pre-paring by distilling equal weights of amyl alcohol and phosphorus pentachloride, washing the product repeatedly with alkaline water, and rectifying with calcium chloride. Less pure it may be obtained by saturating amyl alcohol with hydrochloric acid. It is a colorless liquid, of agreeable odor, insoluble in water, and neutral to test-paper: it boils at $15.6^\circ C.$ ($59.9^\circ F.$), and ignites readily, burning with a flame green at the base. By the long continued action of chlorine, aided by powerful heat, it is converted into octochlorinated amyl chloride, or octopentane, $C_5H_3Cl_8$, a volatile, colorless liquid, smelling of chloroform. The whole of the hydrogen has not yet, however, been removed. The bromide, $C_5H_{11}Br$, is a volatile, colorless liquid, heavier than water, boiling at $119^\circ C.$ ($246.2^\circ F.$). It is obtained by distilling amyl alcohol with bromine and phosphorus (see Ethyl-bromide, p. 569). Its odor is penetrating and alliaceous. The bromide is decomposed by an infusion of potash, with reproduction of the alcohol and formation of potassium bromide. The iodide, $C_5H_{11}I$, is prepared by distilling a mixture of amyl alcohol, 8 of iodine, and 1 of phosphorus. It is a colorless liquid, heavier than water, volatile without decomposition, boiling at $294.8^\circ C.$ ($552.6^\circ F.$), and in other respects resembles the bromide: it is decomposed by exposure to light. Heated to $290^\circ C.$ ($554^\circ F.$) in a glass tube, with zinc, it yields decane or diamyl, $C_{10}H_{22}$, or a colorless ethereal liquid boiling at $155^\circ C.$ ($311^\circ F.$). At the same time there is formed a compound of zinc iodide with zinc amylide, which is decomposed by contact with water, yielding zinc oxide and amyl hydride (p. 499):



AMYL OXIDE, $(C_5H_{11})_2O$, obtained by the processes already mentioned, is a colorless, oily liquid, of specific gravity 0.779, and boiling at $176^\circ C.$ ($346.8^\circ F.$).

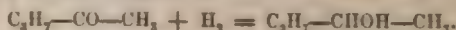
AMYL SULPHATE, or SULPHAMYLIC ACID, $(C_5H_{11})HSO_4$, or $C_5H_{11}(OSO_3H)$. A salt of this acid, $(C_5H_{11})_2Ba(SO_4)_2 \cdot 2Aq.$, prepared like the one (p. 573), crystallizes, on evaporating the solution, in small, white, platy crystals; the difference of solubility of the salts prepared from optically active and optically inactive amyl alcohol has already been

mentioned. The barium may be precipitated from the salt by dilute sulphuric acid, and the sulphanilic acid concentrated by spontaneous evaporation to a syrupy, or even crystalline state: it has an acid and bitter taste, strongly reddens litmus-paper, and is decomposed by ebullition into amyl alcohol and sulphuric acid. The potassium salt forms groups of small radiating needles, very soluble in water. The sulphanilates of calcium and lead are also soluble and crystallizable.

Amyl hydrosulphide, $C_5H_{11}SH$, and Amyl sulphide ($C_5H_{11}S$), resemble the ethyl-compounds in their properties and reactions.

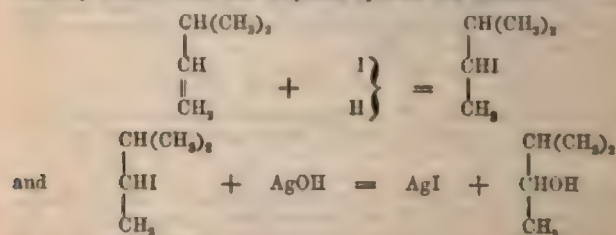
Fusel-oil of Grain-spirit.—The fusel-oil, separated in large quantities from grain-spirit by the London rectifiers, consists chiefly of amyl alcohol mixed with ethyl alcohol and water. Sometimes it contains in addition more or less of the ethyl- or amyl-compounds of certain fatty acids thought to be identical with cinnanthic and palmitic acids. These last-named substances form the principal part of the nearly solid fat produced in this manner in whiskey distilleries conducted on the old plan. Mulder has described, under the name of *corn-oil*, another constituent of the crude fusel-oil of Holland: it has a very powerful odor, resembling that of some of the umbelliferous plants, and is unaffected by solution of caustic potash. According to Mr. Rowney, the fusel-oil of the Scotch distilleries contains in addition a certain quantity of capric acid, $C_{10}H_{20}O_2$. Amyl alcohol, in addition to isobutyl alcohol, has been separated from the spirit distilled from beet-molasses and from artificial grape-sugar made by the aid of sulphuric acid.

Propyl-methyl Carbinol, $HO.HC \begin{smallmatrix} CH_2CH_2CH_3 \\ | \\ CH_3 \end{smallmatrix}$, or, $C_3H_7-CHOH-CH_3$.—This secondary alcohol is produced by decomposing propyl-methyl ketone (obtained by distilling a mixture of calcium butyrate and acetate) with water and sodium amalgam:



It is a liquid smelling like ordinary amyl alcohol, but less pungent; boils at $120^\circ C.$ ($248^\circ F.$); has a specific gravity of 0.825 at 0° ; is oxidized by potassium permanganate to propyl-methyl ketone.

Isopropyl-methyl Carbinol, $HO.HC \begin{smallmatrix} CH(CH_3)_2 \\ | \\ CH_3 \end{smallmatrix}$, also called **Amylene hydrate**, (C_5H_{10}) $\begin{smallmatrix} H \\ | \\ OH \end{smallmatrix}$.—This is a secondary alcohol produced from amylene, C_5H_{10} , by combining that substance with hydriodic acid, and decomposing the resulting hydriodide, $C_5H_{10}.HI$, with moist silver oxide, whereby silver iodide and amylene hydrate are obtained:



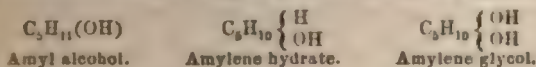
A portion of the hydriodide is at the same time resolved, by the heat evolved in the reaction, into hydriodic acid and amylene; and, on submit-

the resulting liquid to fractional distillation, the amylene passes over, and then, between 105° and 108° C. (221 – 226.4° F.), the amylene rate or isopropylmethyl carbinol.

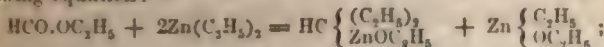
This alcohol is a liquid having a specific gravity of 0.829 at 0° , and a faint ethereal odor, quite distinct from that of ordinary amyl alcohol. Treated with strong sulphuric acid, it is converted, not into amylsulphuric, but into hydrocarbons polymeric with amylene, viz., diamylene, or ne, $C_{10}H_{20}$, and triamylene, or pentadecene, $C_{15}H_{30}$ (p. 505). Hydriodic acid converts it, at ordinary temperatures, into amylene hydriodide, $C_5H_{10}I$, boiling at 130° C. (266° F.), amyl iodide at 146° C. (294.8° F.). Hydriodic acid converts it (even at 0°) into amylene hydrochloride, $C_5H_{10}Cl$, having a boiling point 10° below that of amyl chloride. On mixing with two atoms of bromine at a very low temperature, a red liquid is formed, which, as soon as it attains the ordinary temperature of the air, dissolves into water and amylene bromide. Heated for some time to 100° with strong acetic acid, it yields amylene, together with a small quantity of amylene acetate. Sodium dissolves in amylene hydrate with evolution of hydrogen, forming a colorless translucent mass, which has the composition $C_5H_{10}NaOH$, and is decomposed by amylene hydriodide in the manner shown by the equation:



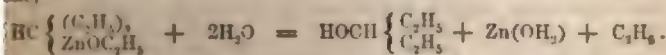
From these reactions it is apparent that amylene hydrate or isopropylmethyl carbinol is especially distinguished from the primary amyl alcohols by the facility with which it gives up the corresponding olefine. This facility is exhibited also by all the secondary alcohols of the series. These alcohols may indeed be regarded as intermediate links between the primary monatomic alcohols and the diatomic alcohols or glycols, e. g.,



Diethyl Carbinol, $C_2H_5-CHOH-C_2H_5$, is produced by heating ethyl hydrate with ethyl iodide and granulated zinc, and decomposing the product with ice-cold water. The action of the zinc on the ethyl iodide produces zinc-ethyl, and this reacts with the ethyl formate according to the following equation:



On treating this product with water, the compound, $HC \left\{ \begin{Bmatrix} C_2H_5 \\ ZnOC_2H_5 \end{Bmatrix} \right.$ is decomposed, yielding diethyl carbinol, together with zinc hydroxide and ethane,



The final result is the replacement of the oxygen-atom of the group HO , formic acid, $HCO.OH$, by 2 atoms of ethyl.

Diethyl carbinol is a liquid which smells like amyl alcohol, has a specific gravity of 0.832 at 0° , and boils at 116 – 117° C. (240.8 – 242.6° F.). By distillation with chromic acid, it is converted with diethyl ketone, $CO(C_2H_5)_2$; the corresponding iodide boils at 145° ; the acetate at 132° .*

* Wagner, Liebig's Annalen, clxxv. 361; Chem. Soc. Journ. 1876, p. 627.

Ethyl-dimethyl Carbinol, or Tertiary Amyl Alcohol,

$C \begin{cases} C_2H_5 \\ (CH_3)_2 \\ OH \end{cases}$, is prepared like tertiary butyl alcohol, by treating these with propionyl chloride, C_2H_5OCl , and decomposing the product with water. It smells very much like tertiary butyl alcohol, has a specific gravity of 0.828 at 0° , solidifies to a crystalline mass at $-30^\circ C.$ ($-22^\circ F.$), boils between 98.5° and $100^\circ C.$ (209.3° and $212^\circ F.$), and does not solidify at $-17^\circ C.$ ($1.4^\circ F.$), but merely becomes viscid. By oxidation with dilute chromic acid, it yields nothing but acetic acid.

The boiling points of the six known pentyl alcohols become gradually lower, from the normal primary to the tertiary, as their structure becomes more complex; thus—

| | | Boiling Point |
|------------|---------------------------------|---------------|
| Primary, | Butyl carbinol . . . | 137° |
| | Isobutyl carbinol . . . | 128°–132° |
| | Propyl-methyl carbinol . . . | 126°–127° |
| Secondary, | Diethyl carbinol . . . | 116°–117° |
| | Isopropyl-methyl carbinol . . . | 104°–106° |
| Tertiary, | Ethyl-dimethyl carbinol . . . | 98.5°–100° |

HEXYL ALCOHOLS AND ETHERS.

The number of possible modifications of an alcohol increases with the number of carbon-atoms in its molecular formula. Thus, we have seen that there may be two propyl alcohols, C_3H_7O , four butyl alcohols, C_4H_9O , and eight amyl alcohols, $C_5H_{11}O$. The six-carbon formula, $C_6H_{13}O$, will in like manner be found to include seventeen isomeric alcohols—eight primary, six secondary, and three tertiary; but as the manner in which these modifications arise has been sufficiently explained in the preceding pages, the further development of the theoretical formula may be left as an exercise for the student.

The number of modifications of the six-carbon alcohol actually known is eight, of which two are primary, three secondary, and the remaining three tertiary.

Primary Hexyl Alcohol, $C_6H_{13}(OH)$.—The normal alcohol, $CH_3CH_2CH_2CH_2CH_2CH_2OH$, or $H_2C \begin{cases} C_4H_9OH \\ CH_2 \end{cases}$, is obtained from the essential oil of *Heracleum giganteum*, which is a mixture of hexyl butyl and octyl acetate. The hexyl and octyl alcohols are isolated by decomposing the oil with alcoholic potash, and separated by fractional distillation. The hexyl alcohol thus obtained has a strong aromatic odor, a specific gravity of 0.819 at $23^\circ C.$ ($73.4^\circ F.$), and boils at $156.0^\circ C.$ ($312.8^\circ F.$). By oxidation it yields a caproic acid, $C_6H_{11}O_2$, having the same boiling point ($204.5^\circ C.$, $400.1^\circ F.$), as normal caproic acid. The corresponding ether is a heavy colorless liquid, boiling at $179.5^\circ C.$ ($355.1^\circ F.$). The acetate, $C_6H_{13}C_2H_3O_2$, has a pleasant fruity odor, and boils at $189^\circ C.$ ($372.2^\circ F.$).

The same alcohol is obtained, together with butyl-methyl carbinol, by treating normal hexane, $CH_3(CH_2)_4CH_3$, from American petroleum, with chlorine, converting the resulting hexyl chloride into the acetate to prevent action with silver acetate, and distilling this acetate with potash. The

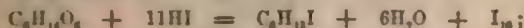
re of alcohols thus obtained cannot be completely separated by fractional distillation, but it yields by oxidation the corresponding products, normal caproic acid and methyl-butyl ketone.

By, normal hexyl alcohol is obtained, according to Rossi, by the action of sodium-amalgam and water on normal caproic aldehyde.

Other primary hexyl alcohol, boiling at about 150°C . (302°F .), and isopropyl caproic acid by oxidation, was found by Faget in fusel-oil. The results respecting it are not very exact, but as it is produced by fermentation, it is probably the isopropyl alcohol, $\text{HC} \begin{cases} \text{C}_2\text{H}_5\text{OH} \\ \text{CH}_2 \\ \text{CH}_3 \end{cases}$.

Secondary Hexyl Alcohols.—1. Methyl-butyl Carbinol,

$\text{C} \begin{cases} \text{H}_3 \\ \text{H}_2 \\ \text{H}_3 \end{cases}$, discovered by Wanklyn and Erlenmeyer, is produced by the action of mannite, $\text{C}_6\text{H}_{12}\text{O}_6$ (a saccharine body obtained from manna), with an excess of very strong hydriodic acid, whereby it is converted into methyl-butyl alcohol:—



digesting this compound with silver oxide and water:—



Methyl-butyl carbinol is a viscid liquid, having a pleasant, refreshing odour; it boils at 137°C . (278.6°F .); has a sp. gr. of 0.8327 at 0° , 0.8209 at 60° (140°F .), and 0.7422 at 99°C . (210.2°F .), so that it expands but rapidly by heat. Strong hydrochloric acid converts it into the monochloride, $\text{CHCl} \begin{cases} \text{C}_2\text{H}_5 \\ \text{CH}_2 \\ \text{CH}_3 \end{cases}$, which boils at 120°C . (248°F .), and yields hexene when digested at 100° with alcoholic potash. The monochloride boils at $167\text{--}168^{\circ}\text{C}$. ($332.6\text{--}334.4^{\circ}\text{F}$.).

The alcohol is converted by oxidation with a mixture of potassium dichromate and sulphuric acid into methyl-butyl ketone, $\text{CO} \begin{cases} \text{C}_2\text{H}_5 \\ \text{CH}_2 \\ \text{CH}_3 \end{cases}$, which, when further treated with the oxidising mixture, yields acetic, propionic, and normal butyric acids.

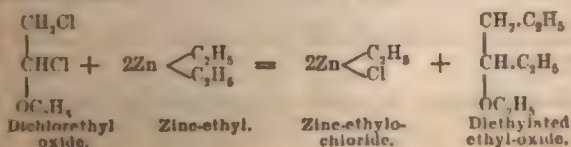
Methyl-katabutyl Carbinol, $\text{HO.HC} \begin{cases} \text{C}(\text{CH}_3)_2 \\ \text{CH}_3 \end{cases}$, also called

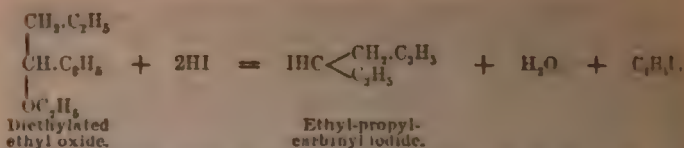
tertiary alcohol, is formed by the action of nascent hydrogen on pinacolin.

It solidifies at low temperatures to crystals which melt at $+4^{\circ}\text{C}$. (39°F .), boils at 120°C . (248°F .), and has a specific gravity of 0.834. Oxidized by potassium dichromate and sulphuric acid, it is converted into methyl-katabutyl ketone, $\text{CH}_3\text{—CO—C}(\text{CH}_3)_2$, which splits on further oxidation into carbon dioxide and trimethylacetic acid.

Ethyl-propyl Carbinol, $\text{HO.HC} \begin{cases} \text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{CH}_2\text{CH}_3 \end{cases}$, also called

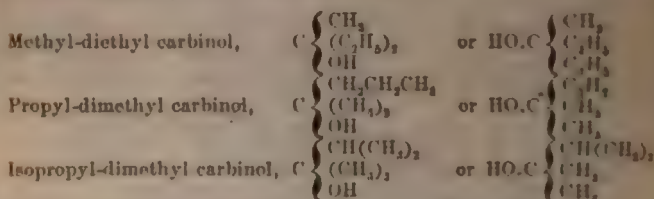
tertiary alcohol.—The iodide analogous to this alcohol is prepared from dichloro-ethyl chloride, $\text{O} \begin{cases} \text{C}_2\text{H}_5\text{Cl}_2 \\ \text{C}_2\text{H}_5 \end{cases}$, by successive treatment with zinc-ethyl and ethyl iodide; thus:





and the alcohol is obtained by converting the iodide into the acetate, and distilling the latter with potash.

Tertiary Hexyl Alcohols.—Three of these alcohols are possible, and have been obtained, viz.:



The first is prepared by treating acetyl chloride, COCH_3Cl , with methyl-ethyl, and decomposing the resulting methyl-diethyl-chloromethane $\text{C}(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{Cl}$, with water. It boils at 120°C . (248°F .), and yields by oxidation nothing but acetic acid.

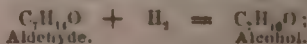
The second, obtained in like manner from butyryl chloride, $\text{CO}(\text{C}_2\text{H}_5)_2\text{Cl}$, and zinc-methyl, boils at 115°C . (239°F .), and is resolved by oxidation into acetic acid, propionic acid, and carbon dioxide.

The third, obtained from isobutyryl chloride and zinc-methyl, is a liquid which solidifies at -35°C . (-31°F .), boils at 112°C . (233.6°F .), and yields by oxidation acetone, acetic acid, and carbon dioxide.

HEPTYL ALCOHOLS, $\text{C}_7\text{H}_{15}\text{OH}$.

Of these alcohols six have been obtained, two primary, one secondary, and three tertiary.

Normal Heptyl Alcohol, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH}$, or $\text{H}_7\text{C} \begin{array}{c} \text{C}_6\text{H}_{13}\text{OH} \\ \diagup \quad \diagdown \\ \text{H}_2 \end{array}$, prepared, either by the action of nascent hydrogen (evolved by the action of sodium-amalgam on water), on heptyl aldehyde (onanthal):



or from normal heptane, C_7H_{16} , in the same manner as normal hexyl alcohol from hexane (p. 588). It is a colorless, oily liquid, insoluble in water, boiling at 177°C . (350.6°F .), and converted by oxidation into normal heptanoic acid.

Another heptyl alcohol, probably the *isoprimary*, was separated by Fieser from fusel-oil.

Secondary Heptyl Alcohol, or **Dipropyl Carbinol**, $\text{C}_3\text{H}_7\text{—CH(OH)—C}_3\text{H}_7$, prepared by hydrogenation of dipropyl ketone, boils at 138°C . (302°F .), and is converted into the ketone by oxidation.

tertiary Heptyl Alcohols.—*Trithyl Carbinol*, $(C_2H_5)_3COH$, is obtained by treating propionyl chloride, C_2H_5COCl , with zinc-methyl, and product with water. It remains liquid at $-20^\circ C.$ ($-4^\circ F.$), boils at $142^\circ C.$ ($284^\circ-287.6^\circ F.$), is slightly soluble in water, and has a sp. gravity of 0.8593 at 0° . By oxidation with chromic acid it yields *lene*, C_7H_{14} , together with carbon dioxide, and apparently also acetic and propionic acids.

Dimethyl-isobutyl Carbinol, $\left. \begin{matrix} C_6H_{13} \\ (CH_3)_2 \end{matrix} \right\} COH$, obtained by treating *aleric chloride*, $CH(CH_3)_2-CH_2-COCl$, with zinc-methyl, and decomposing the product with water, boils at $129^\circ-131^\circ C.$ ($264.2^\circ-267.8^\circ F.$), is converted by oxidation into acetic and isobutyric acids.

Dimethyl-katabutyl Carbinol, or *Pentamethylated Ethyl Alcohol*, $\left. \begin{matrix} H_{12} \\ (CH_3)_2 \end{matrix} \right\} COH$, prepared by treating trimethyl-acetyl chloride, $C(CH_3)_3$, with zinc-methyl, and the product with water, melts at $17^\circ C.$ ($60^\circ F.$), boils at $131^\circ-132^\circ C.$ ($267.8^\circ-269.6^\circ F.$), and forms with water a crystalline hydrate, $2C_7H_{16}O.H_2O$, which melts at $83^\circ C.$ ($181.4^\circ F.$).

OCTYL ALCOHOLS, $C_8H_{17}OH$.

Four of these alcohols are known—one primary, three secondary, and tertiary.

Primary Octyl Alcohol or Heptyl Carbinol, $C_7H_{15}.CH_2OH$, is obtained, together with the corresponding acetate, $C_8H_{17}.C_2H_3O_2$, in the volatile oil obtained from the seed of the cow-parsnep (*Heracleum sphondylium*); as a butyric ether in the seeds of the common parsnep (*Pastinaca sativa*); and, together with hexyl butyrate, in the oil of *Heracleum giganteum*.

The comparatively small portion of cow-parsnep oil, which boils between 180° and 195° , consists mainly of the alcohol; but by far the greater portion passes over between 200° and $212^\circ C.$ (392° and $413.6^\circ F.$), and this, by continued fractionation, yields primary octyl acetate, $C_{10}H_{20}O_2$, boiling between 206° and $208^\circ C.$ ($402.8^\circ-406.4^\circ F.$). This compound is insoluble in water, easily soluble in alcohol and ether, and has a sp. gr. of 0.8717 at $20^\circ C.$ ($68^\circ F.$). Heated with alcoholic potash, it yields potassium acetate and primary octyl alcohol.

The alcohol is a colorless oily liquid, having a sp. gr. of 0.830 at $16^\circ C.$ ($60^\circ F.$), boiling between $190^\circ C.$ ($374^\circ F.$) and $192^\circ C.$ ($377.6^\circ F.$), is insoluble in water, miscible with alcohol and ether; it has a peculiar pungent aromatic odor, and tastes sweetish at first, afterwards burning and sharp. By boiling with potassium dichromate and dilute sulphuric acid it is converted into an acid, $C_8H_{16}O_2$, melting at 16° to $17^\circ C.$ (62.6° to $62.6^\circ F.$) and isomeric or identical with the caprylic acid of natural fats, together with the corresponding octylic ether, $C_8H_{17}.C_8H_{15}O_2$. This reaction leads to it to be a primary alcohol; and from the boiling point of the octane obtained from it ($122^\circ-125^\circ C.$) ($251.6^\circ-257^\circ F.$),* Schorlemmer infers

that normal pentane, C_5H_{12} , boils at $38^\circ C.$ ($100.4^\circ F.$), and the average difference of boiling point between any two consecutive members of the normal paraffin series is $31^\circ C.$ ($87.8^\circ F.$) (p. 591); hence the boiling point of normal octane should be $3 \times 31 + 38^\circ C.$ ($267.8^\circ F.$). On the other hand, isopentane boils at $30^\circ C.$ ($86^\circ F.$), and the difference of boiling point between two consecutive isoparaffins is about $31^\circ C.$ ($87.8^\circ F.$): hence the boiling point of iso-octane should be $3 \times 31 + 123^\circ = 123^\circ$. (Schorlemmer, *Proceedings of the Royal Society*, xvi. 376; also Watts's Dictionary of Chemistry, First Supplement, p. 579.)

that it is an iso-alcohol, $\text{HC} \begin{Bmatrix} \text{C}_6\text{H}_{10}\text{OH} \\ (\text{CH}_3)_2 \end{Bmatrix}$

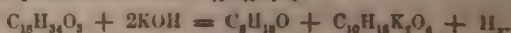
The haloïd octyl ethers obtained from this alcohol exhibit the following properties:

| | Boiling Point. | Sp. gr. |
|--|---------------------------------|---------------------------|
| Chloride, $\text{C}_8\text{H}_{17}\text{Cl}$. . . | 170.5°-180° C. (335.1°-345° F.) | 0.8902 at 10° C. (50° F.) |
| Bromide, $\text{C}_8\text{H}_{17}\text{Br}$. . . | 195°-200° C. (383.4°-392° F.) | 1.1116 " " |
| Iodide, $\text{C}_8\text{H}_{17}\text{I}$. . . | 220°-225° C. (428°-431.6° F.) | 1.1335 " " |

Primary octyl alcohols, convertible by oxidation into caprylic acids, are also obtained from octane; they differ from the alcohol obtained from kerosene oil, but their exact structure has not been ascertained.

Secondary Octyl Alcohols.—1. Methyl-hexyl Carbinol,

$\text{HO.HC} \begin{Bmatrix} \text{C}_6\text{H}_{13} \\ \text{CH}_3 \end{Bmatrix}$, is produced by heating castor-oil with excess of solid potassium hydroxide. Castor-oil contains ricinoleic acid, $\text{C}_{18}\text{H}_{33}\text{O}_2$, and the acid, when heated with potash, yields free hydrogen, a distillate containing methyl-hexyl carbinol, together with products of its decomposition, and a residue of potassium sebate, $\text{C}_{10}\text{H}_{18}\text{K}_2\text{O}_4$:

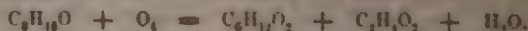


To separate the alcohol, the distillate is repeatedly rectified over fused potash, the portion boiling below 200° C. (392° F.) only being collected; this liquid, subjected to fractional distillation yields a portion boiling at 181° C. (357.8° F.), which is the pure secondary octyl alcohol. The portions of the original distillate having a lower boiling point, consist of olefines, amongst which octene, C_8H_{16} , boiling at 150° C. (302° F.), preponderates.

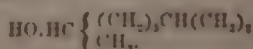
The same alcohol is obtained from the octane of American petroleum, by converting this hydrocarbon into octyl chloride, then into the acetate, and heating the latter with alcoholic potash.

Methyl-hexyl carbinol is a limpid oily liquid, having a strong acrolein-odor, and making grease-spots on paper. It has no action on polarized light. It has a specific gravity of 0.823 at 17° C. (62.6° F.), and boils at 181° C. (357.8° F.). It is insoluble in water, but dissolves in alcohol, ether, wood-spirit, and acetic acid. It mixes with sulphuric acid, forms octyl-sulphuric acid, $\text{C}_8\text{H}_{17}\text{HSO}_4$, generally also octene and neutral octyl sulphate. Fused zinc chloride converts it into octene. With potassium and sodium it yields substitution-products.

Methyl-hexyl carbinol, oxidized with potassium dichromate and sulphuric acid, yields the corresponding ketone, viz., methyl-hexyl ketone, $\text{CH}_3\text{—CO—C}_6\text{H}_{13}$, and by the prolonged action of the oxidizing mixture, this ketone is further oxidized to caproic and acetic acids:

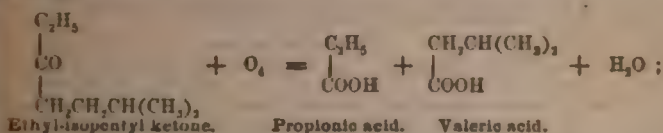


These reactions show that the alcohol produced from castor-oil is a secondary alcohol; and from considerations similar to those above adduced with respect to the primary alcohol, it is inferred to be a secondary iso-alcohol represented by the formula:



The Chloride, $\text{C}_8\text{H}_{17}\text{Cl}$, produced by the action of phosphorus pentachloride on this alcohol, has an odor of oranges, a specific gravity of 0.890 at 18° C. (64.4° F.), and boils at 175° C. (347° F.). Heated with alcoholic potash, it yields octene, C_8H_{16} ; by alcohol and potassium acetate, it is converted into octene and octyl acetate.

2. *Ethyl-isopentyl Carbinol*, $\text{HO.CH} \left\{ \begin{array}{l} \text{CH}_2\text{CH}_3 \\ (\text{CH}_2)_2\text{CH}(\text{CH}_3)_2 \end{array} \right.$, is obtained, together with the primary alcohol, from the octane produced by the action of zinc and hydrochloric acid on the secondary octyl iodide obtained from the alcohol last described. The octyl chloride prepared from this octane smells faintly of oranges, and the acetate prepared from it yields, when heated with alcoholic potash, an octyl alcohol, which boils at $182\text{--}186^\circ \text{C.}$ ($359.6\text{--}366.8^\circ \text{F.}$), and is converted by oxidation into a ketone, $\text{C}_8\text{H}_{16}\text{O}$, isomeric with methyl-hexyl ketone, but differing from it by yielding, when further oxidized, not caproic and acetic, but propionic and ordinary valeric acid: hence, it consists of ethyl-isopentyl ketone (see KETONES):



and the alcohol from which it is obtained is ethyl-isopentyl carbinol.

3. A secondary octyl alcohol, different from both the preceding, has been obtained from octene, by heating this hydrocarbon in a sealed tube with hydriodic acid, converting the resulting octyl iodide, or octene hydriodide, $\text{C}_8\text{H}_{18}\text{HI}$, into the acetate, and distilling the latter with finely pulverized potassium hydroxide. This alcohol has an aromatic odor, a specific gravity of 0.811 at 0°C. (32°F.), and boils at $174\text{--}178^\circ \text{C.}$ ($345.2\text{--}352.4^\circ \text{F.}$). By oxidation it yields the same products as the castor-oil alcohol, and must therefore likewise consist of methyl-hexyl carbinol; but as it boils at a lower temperature than the latter, it probably contains a different modification of hexyl.

Tertiary Octyl Alcohol, or Propyl-diethyl Carbinol,

$\text{HO.C} \left\{ \begin{array}{l} \text{C}_3\text{H}_7 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right.$, is formed by treating butyryl chloride, $\text{C}_4\text{H}_7\text{COCl}$, with zinc-ethyl, and decomposing the product with water. It is a somewhat viscid liquid, lighter than water, and insoluble therein, and does not solidify in a freezing mixture. With phosphorus pentachloride it yields an octyl chloride boiling at 155°C. (311°F.). By oxidation with chromic acid mixture it yields propionic and acetic acids.

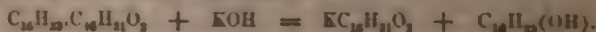
Nonyl Alcohol, $\text{C}_9\text{H}_{19}\text{OH}$, is obtained by the series of reactions above described from the nonane of American petroleum, and likewise occurs, together with the nonene, C_9H_{18} , in that portion of the liquid obtained by distilling amyl alcohol with zinc chloride, which boils between 134°C. (273.2°F.) and 150°C. (302°F.). Nonyl alcohol boils at about 200°C. (392°F.). Nonyl chloride, $\text{C}_9\text{H}_{19}\text{Cl}$, has a specific gravity of 0.899 at 16°C. (60.8°F.), and boils at 196°C. (384.8°F.).

Decyl Alcohol, $\text{C}_{10}\text{H}_{21}\text{OH}$, from petroleum decane, boils at $210\text{--}215^\circ \text{C.}$ ($410\text{--}419^\circ \text{F.}$). An isomeric alcohol, probably tetra-ethylated ethyl alcohol, $\text{CH}(\text{C}_2\text{H}_5)_4\text{—C}(\text{C}_2\text{H}_5)_2\text{OH}$, is formed by the action of dibromacetyl bromide, CHBr.COBr , on zinc-ethyl; it boils at $155\text{--}157^\circ \text{C.}$ ($311\text{--}314.6^\circ \text{F.}$).

The alcohols of the series $\text{C}_n\text{H}_{2n+1}\text{O}$ containing 11 to 15 carbon-atoms,

are not known, but compound ethers containing 12 and 14 carbon atoms appear to occur in spermaceti.

Hexdecyl, or Cetyl Alcohol, $C_{16}H_{34}O = C_{16}H_{33}(OH)$, also called *Ethol*, is obtained from spermaceti, a crystalline fatty substance found in peculiar cavities in the head of the sperm whale (*Physeter macrocephalus*). This substance consists of cetyl palmitate, $C_{16}H_{33}O_2$, or $C_{16}H_{31}O_2$, and when heated for some time with solid potash, is resolved into potassium palmitate and cetyl alcohol:—



The cetyl alcohol is dissolved out from the fused mass by alcohol and ether, and purified by several crystallizations from ether.

Cetyl alcohol, or ethol, is a white crystalline mass, which melts at about $56^\circ C.$ ($132^\circ F.$), and crystallizes by slowly cooling in shining laminae. It has neither taste nor smell, is insoluble in water, but dissolves in all proportions in alcohol and ether. When heated it distils without decomposition. With sodium it gives off hydrogen and yields sodium cetylate, $C_{16}H_{33}NaO$. It is not dissolved by aqueous alkalis; but when heated with a mixture of potash and lime, it gives off hydrogen, and is converted into palmitic acid:—



Distilled with phosphorus pentachloride it yields cetyl chloride, $C_{16}H_{33}Cl$, a limpid oily liquid, having a specific gravity of 0.8412 at $12^\circ C.$ ($53.6^\circ F.$), and distilling with partial decomposition at a temperature above $200^\circ C.$ ($392^\circ F.$). Cetyl iodide, $C_{16}H_{33}I$, obtained by treating the alcohol with iodine and phosphorus, is a solid substance which melts at $22^\circ C.$ ($71.6^\circ F.$), dissolves in alcohol and ether, and crystallizes from alcohol in interlaced laminae.

According to Heintz, cetyl alcohol, or ethol, prepared as above, is not a definite compound, but a mixture of hexdecyl alcohol, $C_{16}H_{33}O$, and small quantities of three other alcohols of the same series, containing respectively 12, 14, and 18 atoms of carbon, inasmuch as, when fused with potash-lime, it yields the corresponding fatty acids, $C_{16}H_{33}O_2$.

Ceryl Alcohol, $C_{27}H_{54}O = C_{27}H_{53}(OH)$; also called *Cerotic alcohol* and *Cerotin*.—This alcohol is obtained from Chinese wax or Pella, a secretion enveloping the branches of certain trees in China, and supposed to be produced by the puncture of an insect. This wax consists mainly of ceryl cerotate, $C_{27}H_{53}O_2$, and is decomposed by fused potash in the same manner as spermaceti, yielding potassium cerotate and ceryl alcohol:—



On digesting the fused mass with boiling water, a solution of potassium cerotate is obtained, holding ceryl alcohol in suspension; and on precipitating the cerotic acid with barium chloride and treating the resulting precipitate with alcohol, the ceryl alcohol dissolves, and may be purified by repeated crystallization from alcohol or ether. It then forms a waxy substance, melting at $97^\circ C.$ ($206.6^\circ F.$). Heated with potash-lime, it gives off hydrogen, and is converted into potassium cerotate. At very high temperatures it distils, partly undecomposed, partly resolved into water and cerotone, $C_{27}H_{52}$; by this character it would appear to be related to the secondary alcohols. With sulphuric acid in excess, it forms hydrated neutral ceryl sulphate, $(C_{27}H_{50})_2SO_4.H_2O$.

Myricyl Alcohol.— $C_{30}H_{62}O = C_{30}HO_{61}(OH)$.—This alcohol, the highest known member of the series, $C_nH_{2n+2}O$, is obtained from myricin, the portion of common bees' wax which is insoluble in boiling alcohol. Myricin consists of myricyl palmitate, $C_{30}H_{61}.C_{16}H_{31}O_2$, and when heated with potash is decomposed in the same manner as spermaceti and Chinese wax, yielding potassium palmitate and myricyl alcohol. On dissolving the product in water, precipitating with barium chloride, exhausting the precipitate with boiling alcohol, and dissolving the substance deposited from the alcohol in light petroleum, pure myricyl alcohol separates as a crystalline substance, having a silky lustre. When heated, it partly sublimes unaltered, and is partly resolved (like ceryl alcohol) into water and melene, $C_{30}H_{60}$. With strong sulphuric acid it yields myricyl sulphate. Heated with potash-lime, it gives off hydrogen, and is converted into potassium melissate:



The mother-liquor from which the myricyl alcohol has crystallized out, as above mentioned, retains a small quantity of an isomeric alcohol, which melts at $72^\circ C$. ($161.6^\circ F.$), and when treated with potash-lime yields an acid containing a smaller proportion of carbon.

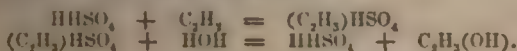
2. Monatomic Alcohols, $C_nH_{2n}O$, or $C_nH_{2n-1}OH$.

Two alcohols of this series are known, viz.:

Vinyl alcohol, $C_2H_4O = C_2H_3(OH)$

Allyl alcohol, $C_3H_6O = C_3H_5(OH)$.

The first, discovered by Berthelot in 1860, is produced by combining ethine or acetylene with sulphuric acid, whereby vinyl sulphuric acid $(C_2H_3)HSO_4$ is formed, and distilling the product with water, just as in the preparation of ethyl alcohol from ethene:



It is an easily decomposable liquid, having a highly pungent odor, somewhat more volatile than water, soluble in 10 to 15 parts of that liquid, and precipitated from the solution by potassium carbonate. It is isomeric with acetic aldehyde and ethene oxide (p. 620). The univalent radicle vinyl, C_2H_3 , which may be supposed to exist in it, is related to the trivalent radicle ethenyl (p. 479) in the same manner as allyl to propenyl (see below).

$$\begin{array}{c} CH_2 \\ || \\ CH \\ | \\ CH_2OH \end{array}$$

Allyl Alcohol, $C_3H_6O = C_3H_5(OH)$.—This alcohol, dis-

covered by Cahours and Hofmann in 1856, may be supposed to contain the univalent radicle allyl, C_3H_5 , derived from a saturated hydrocarbon by abstraction of one atom of hydrogen, and isomeric with the trivalent radicle propenyl, (C_3H_5) , derived from propane, $CH_3-CH_2-CH_3$, by abstraction of three atoms of hydrogen. Allyl and propenyl compounds, indeed, are easily converted one into the other by addition or subtraction of two atoms of a monad element or radicle.

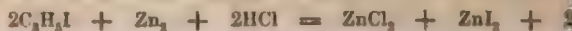
Allyl alcohol is a colorless liquid, having a pungent odor and a burning taste. It mixes in all proportions with water, common and ether; boils at 103°C . (217.4°F .); burns with a brighter common alcohol.

Allyl alcohol is a primary alcohol, similar in all its ordinary to ethyl alcohol. By oxidation in contact with platinum black quickly by treatment with potassium dichromate and sulphuric converted into acrylic aldehyde (acrolein), $\text{C}_3\text{H}_4\text{O}$, and acrylic acid compounds related to it in the same manner as common aldehyde acid to ethyl alcohol. Heated with phosphoric oxide, it yields C_3H_4 . With potassium and sodium it yields substitution-product sulphuric acid converts it into allyl-sulphuric acid. With the and chlorides of phosphorus it yields allyl bromide, $\text{C}_3\text{H}_5\text{Br}$, chloride, $\text{C}_3\text{H}_5\text{Cl}$.

ALLYL BROMIDES.—The *monobromide*, $\text{C}_3\text{H}_5\text{Br}$, prepared as just or by distilling propene bromide, $\text{C}_3\text{H}_5\text{Br}_2$, with alcoholic potash, of specific gravity 1.47, and boiling at 62°C . (143.6°F .). A of allyl, $\text{C}_3\text{H}_5\text{Br}_3$, is obtained by adding bromine to the mono- vessel surrounded by a freezing mixture. It is a liquid of specific 1.436 at 23°C . (73.4°F .), boiling at 217°C . (422.6°F .), and when cooled below 10°C . (50°F .). It is isomeric with propene or tribromhydrin, obtained by the action of phosphorus pentab glycerin.

A *diallyl tetrabromide*, $\text{C}_6\text{H}_{10}\text{Br}_4$, is formed by the direct comb diallyl (p. 513), with bromine; it is a crystalline body, melting (98.6°F .).

ALLYL IODIDES.—The *mono-iodide*, $\text{C}_3\text{H}_5\text{I}$, obtained, as above by distilling glycerin with phosphorus triiodide, is a liquid gravity 1.780 at 16°C . (60.8°F .), and boiling at 100°C . (212 is decomposed by sodium, with formation of diallyl, C_6H_{10} . By of zinc or mercury and hydrochloric or dilute sulphuric acid verted into propene (or allyl hydride):—



ALLYL SULPHIDE, $(C_3H_5)_2S$.—This compound exists, together with a small quantity of allyl oxide, in volatile oil of garlic, and is formed artificially by distilling allyl iodide with potassium monosulphide:—



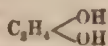
It is prepared from garlic, the sliced bulbs are distilled with water, and the crude oil thus obtained—which is a mixture of the sulphide and oxide of allyl—is subjected to the action of metallic potassium, renewed until it no longer tarnishes, whereby the allyl oxide is decomposed, after which the sulphide may be obtained pure by re-distillation. In this state it is a colorless liquid, lighter than water, of high refractive power, possessing in a high degree the peculiar odor of the plant, and distilling without decomposition. Allyl sulphide, dissolved in alcohol and mixed with solutions of platinum, silver, and mercury, gives rise to crystalline compounds, consisting of a double sulphide of allyl and the metal, either pure or mixed with a double chloride.

Volatile Oil of Mustard, consisting essentially of allyl isothiocyanate, C_3H_5CNS , is described in connection with the thiocyanic ethers (p. 547).

Allyl Hydrosulphide, or Allyl Mercaptan, $C_3H_5(SH)$, obtained by distilling allyl iodide with potassium hydrosulphide, is a volatile oily liquid, having an odor like that of garlic oil, but more ethereal, boiling at $30^\circ C.$ ($86^\circ F.$). It attacks mercuric oxide like ethyl mercaptan, forming a compound $Hg(C_3H_5)_2S_2$.

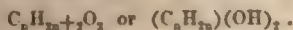
DIATOMIC ALCOHOLS AND ETHERS.

The diatomic alcohols are derived from saturated hydrocarbons by substitution of two equivalents of hydroxyl for two atoms of hydrogen, and they therefore be regarded as compounds of bivalent radicles with two equivalents of hydroxyl: ethene alcohol, for example, may be represented either of the formulae:—



the first representing it as a derivative of ethane, $\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array}$; the second as a compound of ethene, C_2H_4 , with hydroxyl, or as derived from a double molecule of water, $H_2(OH)_2$, by substitution of ethene for two atoms of hydrogen.

The diatomic alcohols of the fatty group, called glycols, are represented by the general formula—

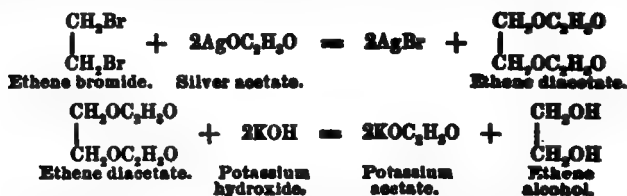


They may be regarded as compounds of olefines with two equivalents of hydroxyl. The following are known:—

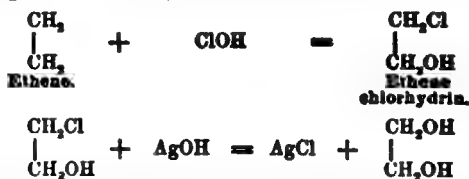
| | |
|--------------------------------------|----------------------------------|
| Ethene alcohol | $C_2H_6O_2 = C_2H_4(OH)_2$ |
| Propene alcohol | $C_3H_8O_2 = C_3H_6(OH)_2$ |
| Tetrene or Butene alcohol | $C_4H_{10}O_2 = C_4H_8(OH)_2$ |
| Pentene or Amylene alcohol | $C_5H_{12}O_2 = C_5H_{10}(OH)_2$ |
| Octene alcohol | $C_8H_{18}O_2 = C_8H_{16}(OH)_2$ |

The glycols are formed by the following processes :—

1. By combining an olefine with bromine ; treating the resulting di-bromide with an alcoholic solution of potassium acetate, or with silver acetate, whereby it is converted into a diacetate of the olefine ; and decomposing this compound with solid potassium hydroxide, whereby potassium acetate and a diatomic alcohol are formed, the latter of which may be distilled off :—



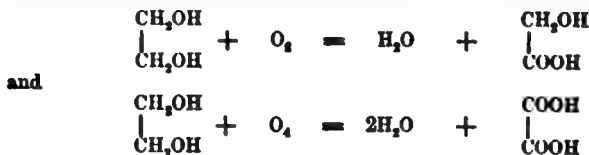
2. By combining an olefine with hypochlorous acid, and treating the resulting compound (a chlorhydrin) with moist silver oxide :



Properties.—The glycols are colorless, inodorous, more or less viscid liquids, having a sweetish taste, freely soluble in water and alcohol ; ethene alcohol is but sparingly soluble in ether ; the rest dissolve easily in that liquid.

The chemical reactions of the glycols have been studied chiefly in the case of ethene alcohol. They are, for the most part, similar to those of the monatomic alcohols : but inasmuch as the glycols contain two atoms of replaceable hydrogen, or of hydroxyl, the reactions generally take place by two stages, yielding two series of products.

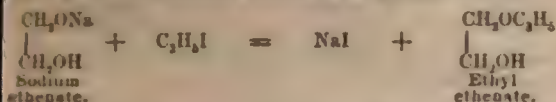
1. Ethene alcohol treated with *nitric acid* gives up 2 or 4 atoms of hydrogen in exchange for oxygen, and is converted into glycollic acid, $\text{C}_2\text{H}_4\text{O}_3$, or oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, according as the action takes place at ordinary or at higher temperatures ; thus :



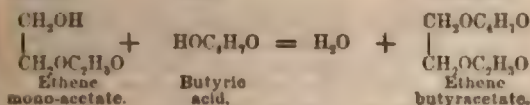
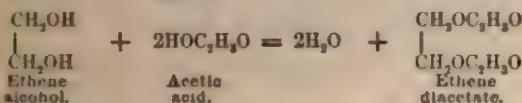
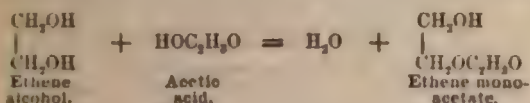
Under certain circumstances the corresponding aldehydes are also produced, as glyoxal, $\begin{array}{c} \text{COH} \\ | \\ \text{COH} \end{array}$, from ethene alcohol, by removal of four hydrogen-atoms without substitution.

2. *Potassium* and *sodium* eliminate one or two atoms of hydrogen from the glycols, and form substituted Ethene alcohol is strongly a

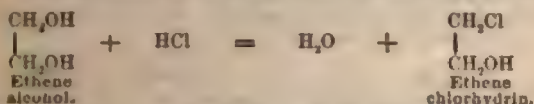
by sodium, yielding sodium ethenate, $C_2H_3NaO_2$; and this end, fused with excess of sodium, is converted into disodium ethenate, $C_2H_2Na_2O_2$. These compounds, treated with monatomic alcohols, yield the alcoholic ethers of the glycols; thus:



Oxygen acids, heated with glycols in closed vessels, act upon them in the same manner as upon the monatomic alcohols, converting them into acid salts or compound ethers, mono-acid or di-acid, according to the proportions used. In the di-acid glycol-ethers, the two radicals in the hydrogen is replaced may belong either to the same or to different acids, *e. g.*,



Haloïd acids (HCl and HBr) act in the same manner as oxygen-acids, but that the reaction never goes beyond the first stage; *e. g.*,



Hydriodic acid, a further action generally takes place, resulting in the liberation of iodine, and the formation of an olefine; thus:



Monochlorhydrins, etc., of the glycols (haloïd hydrins), are formed, as above mentioned, by direct addition of hypochlorous acid to alkenes. When treated with nascent hydrogen, they are converted into monatomic alcohols; *e. g.*,

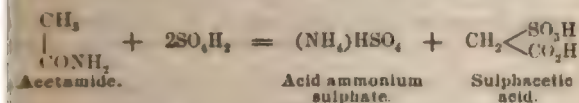


sulphide, is converted into methene sulphide, a body which boils at 218°C . (424°F .), sublimes easily, and yields a vapor whose density (69 referred to hydrogen), shows that the molecule of this compound is not CH_2S , but $\text{C}_2\text{H}_4\text{S}_2$. $\left(\frac{36 + 6 + 96}{2} = 69\right)$. Hence it is inferred that the oxide from which it is formed has also, in the solid state, the constitution represented by the formula $\text{C}_2\text{H}_4\text{O}_3$, or $(\text{CH}_2)_2\text{O}_3$.

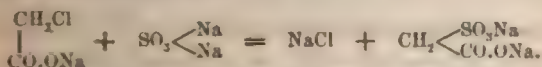
Ethene-disulphonic or Methionic acid, $\text{CH}_2\text{SO}_3\text{H}$, formed by the action of fuming sulphuric acid on acetamide or acetonitril (methyl cyanide, CH_3CN , see below), crystallizes in long deliquescent needles. It is very stable, not being altered by boiling with nitric acid. The barium-salt, $\text{CH}_2(\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$, forms nacreous laminae, sparingly soluble in water; it is precipitated from the aqueous solution of the acid by barium chloride.

Ethene-hydrinsulphonic acid, $\text{CH}_2\text{SO}_3\text{H}$, or *Oxymethyl-sulphonic acid*, is obtained by acting on methyl alcohol with sulphuric anhydride, and diluting the product with water. It crystallizes with difficulty, and is very stable. Its barium salt crystallizes in small anhydrous tables.

Sulphacetic acid, $\text{CH}_2\text{SO}_3\text{H}$ (Methene carbonyl-sulphonic acid), is the chief product of the action of sulphuric acid on acetamide or acetonitril.

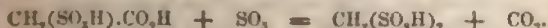


It is also produced by heating a mixture of glacial acetic acid and sulphuric anhydride, and as a sodium salt by boiling a solution of sodium sulphite with sodium monochloroacetate:



Neutralizing the solution obtained by the second process with lead carbonate, and decomposing the solution of the resulting lead-salt with hydrogen sulphide, a solution is obtained which, when concentrated, yields sulphacetic acid in transparent prisms.

Sulphacetic acid is a strong dibasic acid. When heated with sulphuric anhydride, it is converted into methene-disulphonic or methionic acid:



It is also, methionic acid is obtained as the ultimate product of the action of fuming sulphuric acid on acetamide or acetonitril.

Ethene Glycol, $\text{C}_2\text{H}_4\text{O}_2 = \text{C}_2\text{H}_4(\text{OH})_2 = \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$, prepared by di-

hydrolysis of the monoacetate or diacetate of ethene with caustic potash, is a colorless liquid, having a specific gravity of 1.125 at 0° , and boiling at 197°C . (387.5°F .). It mixes freely with water and alcohol, but is slightly soluble in ether. Its reaction with sodium, and the formation

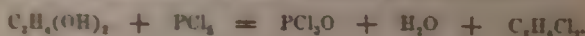
of ethylic ethers by treating the resulting sodium derivatives with ethyl iodide, have been already described (pp. 595, 599).

Ethyle Erienate, $C_2H_5(OH)(OC_2H_5)$, likewise formed by direct combination of ethene oxide with ethyl alcohol, is a liquid having a fragrant odor, and boiling at $127^\circ C.$ ($260.6^\circ F.$). The *diethyle ether*, $C_2H_5(OC_2H_5)_2$, boils at $124^\circ C.$ ($253.4^\circ F.$).

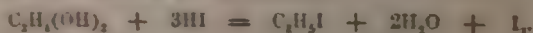
Glycol heated with zinc chloride yields aldehyde :



With phosphorus pentachloride it forms ethene dichloride :



Hydroiodic acid reduces it to ethyl iodide :



Ethene Chlorhydrate or **Ethene Chlorhydrin**, $C_2H_4\begin{array}{c} OH \\ | \\ OH \end{array}$, is formed by heating glycol with hydrochloric acid, or by agitating ether with aqueous hypochlorous acid. It is a colorless liquid, miscible with water, and boiling at $128^\circ C.$ ($262.4^\circ F.$). By oxidation with chromic acid mixture it is converted into monochloroacetic acid :



By heating with potassium iodide it is converted into ethene iodhydrin, $C_2H_4(HO)I$, a viscid liquid, which decomposes when distilled.

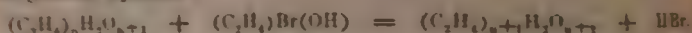
Ethene Nitrate, $C_2H_4(SO_3)_2$, produced by heating ethene iodide with silver nitrate in alcoholic solution, or by dissolving glycol in a mixture of strong nitric and sulphuric acid, is a yellowish liquid, of specific gravity 1.483 at $80^\circ C.$ ($166.4^\circ F.$), insoluble in water, exploding when heated. In alkalis it is resolved into glycol and nitric acid.

Ethene-sulphuric Acid, $C_2H_4SO_3H_2 = SO_2\begin{array}{c} OH \\ | \\ OH \end{array}$, is produced by heating glycol with sulphuric acid. Its barium salt, obtained by neutralizing the oxidel acid solution with barium carbonate, is very soluble, deliquescent, and decomposes when heated with baryta-water into ether and barium sulphate.

Ethene Oxide, C_2H_4O , or $O\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}$, isomeric with acetic aldehyde, is formed by the action of caustic potash on ethene chlorhydrin. The action is violent, and the ethene oxide is given off in vapor, which may be condensed in a receiver surrounded by a freezing mixture, and containing a few lumps of calcium chloride, over which the product may be afterwards dried. It is an ethereal mobile liquid, having a specific gravity of 0.87 at 0° , boiling at $13.5^\circ C.$ ($56.3^\circ F.$) (aldehyde boils at $21^\circ C.$, $69.8^\circ F.$), and is miscible in all proportions with water and with alcohol. When the aqueous solution is treated with sodium amalgam, in a vessel surrounded with a freezing mixture, the ethene oxide takes up hydrogen, and is converted into ethyl alcohol :



and the other polyethenic alcohols are formed, each from the one just below it in the series, by the action of ethene bromhydrin, according to the general equation :



The hydrobromic acid thus formed then acts on the excess of glycol present, reproducing ethene bromhydrin, and thus the action is continued. By this process, the 2-, 3-, 4-, 5-, and 6-ethenic alcohols have been obtained and separated by fractional distillation; and when a sufficient excess of glycol is present, the temperature being kept between $118^\circ C.$ ($240^\circ F.$) and $120^\circ C.$ ($248^\circ F.$), still higher members of the series are produced.

The polyethenic alcohols are syrupy liquids, becoming more viscous as their molecular weight increases; their boiling point rises by about $14^\circ C.$ ($25^\circ F.$) for each addition of C_2H_4O .

Diethenic alcohol, $C_4H_{10}O_2$ or $(C_2H_4)_2H_2O_3$, boils at about $245^\circ C.$ ($473^\circ F.$); the density of its vapor is 3.78 (air = 1); by calculation it should be 4 G., so that it exhibits the normal condensation to two volumes. By action with platinum black, or by treatment with nitric acid, it is oxidized to diglycollic acid, $C_4H_6O_5$, an acid isomeric with malic acid, and formed from diethenic alcohol by substitution of O for H_2 , just as glycolic acid, $C_2H_4O_3$, is formed from monethenic alcohol, $C_2H_4O_1$. *Triethenic alcohol*, $C_6H_{16}O_4$, or $(C_2H_4)_3H_2O_4$, is oxidized in like manner to ethene-diglycollic acid, $C_6H_{12}O_7$.

Ethene Hydrosulphide or Thiohydrate.—*Ethenic or glycolic acetate*, $C_2H_4(SH)_2$, formed by the action of ethene bromide on an alcoholic solution of potassium hydrosulphide, is a colorless oil, of specific gravity 1.12, boiling at $146^\circ C.$ ($294.8^\circ F.$), insoluble in water, soluble in alcohol and ether. With lead acetate it forms a yellow precipitate consisting of $C_2H_4S_2Pb$, and similar compounds with other metallic salts.

Ethene Sulphide, C_2H_4S , formed by the action of ethene bromide on potassium sulphide in alcoholic solution, is a crystalline body, melting at $110^\circ C.$ ($230^\circ F.$), and boiling at $200^\circ C.$ ($392^\circ F.$). Its vapor-density ($H = 1$) is 60, showing that its molecular formula is $(C_2H_4)_2S_2$. Its constitution is therefore $C_2H_4 \begin{smallmatrix} \diagup S \diagdown \\ \diagdown S \diagup \end{smallmatrix} C_2H_4$.

Ethene Hydroxysulphide or Monothio-hydrate, $C_2H_4(OH)(SH)$, formed by the action of ethene chlorhydrin on potassium hydrosulphide, is a liquid of similar properties, and forms salts in which half the hydrogen is replaced by a metal. Nitric acid oxidizes it to isethionio acid, $C_2H_4SO_3$.

Ethene-sulphonic Acids.—*Ethene-disulphonic acid*, $C_2H_4 \begin{smallmatrix} \diagup SO_3H \\ \diagdown SO_3H \end{smallmatrix}$, is formed by oxidation of ethene hydrosulphide, $C_2H_4(SH)_2$, and ethene thiocyanate, $C_2H_4(CNS)_2$, by the action of fuming sulphuric acid on alcohol or ether; and by boiling ethene bromide with a strong solution of potassium sulphite:—



It forms a thick liquid, very soluble in water, difficult to crystallize. The crystallized acid melts at $94^\circ C.$ ($201.2^\circ F.$). The barium salt, $C_2H_4(SO_3)_2Ba$, crystallizes from water in six-sided tables.

Ethene-hydrinsulphonic acid, or *Isethionic acid*, $C_2H_4\begin{smallmatrix} \text{OH} \\ \text{SO}_3H \end{smallmatrix}$, is formed with ethylsulphuric acid, $SO_2\begin{smallmatrix} \text{OH} \\ \text{OC}_2H_5 \end{smallmatrix}$, is produced by the oxidation of ethene mono-thiohydrate, $C_2H_4\begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$, with nitric acid; by the action of nitrous acid on taurine:—



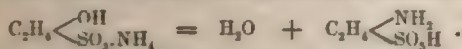
heating ethene-chlorhydrin with potassium sulphite:—



by boiling ethionic acid with water (p. 606).

When vapor of sulphuric anhydride is passed into well-cooled alcohol or ether, and the product is boiled with water for several hours, a solution is formed, containing ethionic, sulphuric, and a small quantity of methionic acid; and on saturating this liquid with barium carbonate, filtering from the barium sulphate, and leaving the filtrate to cool, methionate of barium crystallizes out first, and afterwards the isethionate.

Ethionic acid is a viscid liquid, which does not easily crystallize: it is decomposed by boiling with water. Its salts are stable, and crystallize well. The ammonium salt crystallizes in rhombic plates melting at 100° C. (374° F.); when heated to 210–220° C. (410–428° F.), it is converted into amidethylsulphonic acid or taurine:—



On the action of phosphorus pentachloride on isethionic acid or its salts, phosphor chloride, $C_2H_4Cl.SO_2Cl$, is formed, as a liquid which boils at 200° C. (392° F.), and is converted by boiling with water into chloroethylsulphonic acid, $C_2H_4Cl.SO_3H$.

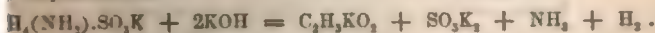
Taurine, $C_2H_4(NH_2).SO_3H$, occurs in combination with cholic acid (as taurocholic acid), in the bile of oxen and other animals, and in various animal secretions. It may be prepared by boiling taurocholic acid with an alkali:—



Taurine is formed artificially, as already observed, by heating ammonium isethionate to 230° C. (446° F.); also by heating chloroethylsulphonic acid with aqueous ammonia.

Taurine crystallizes in large monoclinic prisms, easily soluble in hot water, insoluble in alcohol, melting and decomposing at about 240° C. (464° F.). It forms salts with alkalis, and dissolves in acids, but separates from the solution unaltered.

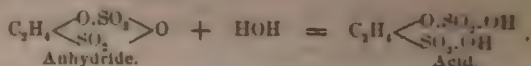
Taurine is not decomposed by boiling with acids or with alkalis, but on fusion with potassium hydroxide it is decomposed in the manner shown by the equation:—



Chlorosulphonic acid converts it into isethionic acid.

Ethionic acid and Anhydride.—The anhydride, $C_2H_4S_2O_4$, formerly called *sulphate of carbyl*, is formed by passing the vapor of sulphur trioxide

into anhydrous alcohol; also by direct union of ethene with sulphur trioxide. It is a very deliquescent crystalline mass, which melts at 86°C . (176°F .). It readily takes up the elements of water, and is converted into ethionic acid, $\text{C}_2\text{H}_4\text{S}_2\text{O}_7$:—



Ethionic acid, having one of its sulphur-atoms connected with a carbon-atom directly, the other only through the medium of oxygen, is both as a sulphonic acid and as an acid ether of sulphuric acid; it is therefore bibasic. Both the free acid and its salts are resolved by boiling with water into sulphuric and isethionic acids :—



ETHIDENE COMPOUNDS.

Ethidene dichloride, $\text{CH}_3\text{—CHCl}_2$, has already been described (p. 518). The *oxide*, $\text{CH}_3\text{—CHO}$, is ordinary aldehyde (see ALDEHYDES).

Ethidene Dimethylate, $\text{CH}_3\text{—CH}(\text{OCH}_3)_2$, occurs in crude wood spirit, and is formed in the oxidation of a mixture of methyl and ethyl alcohols; also by heating aldehyde with methyl alcohol. It is a colorless ethereal liquid, having a specific gravity of 0.8555, and boiling at 69°C . (149°F .).

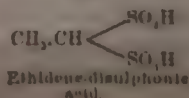
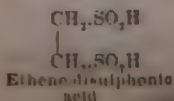
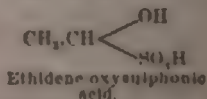
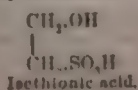
Ethidene Methyl-ethylate, $\text{CH}_3\text{—CH} \begin{array}{c} \text{OCH}_3 \\ \text{OC}_2\text{H}_5 \end{array}$, formed simultaneously with the preceding by the oxidation of a mixture of methyl and ethyl alcohol, boils at 85°C . (185°F .).

Ethidene-Diethylate, or *Acetal*, $\text{CH}_3\text{—CH}(\text{OC}_2\text{H}_5)_2$, isomeric with ethene diethylate, is formed by oxidation of ethyl alcohol, and is found among the first portions of the distillate obtained in the preparation of ordinary spirit. It is formed also by the action of sodium ethylate on ethidene dichloride, and by heating aldehyde with alcohol to 140°C in sealed tubes :—



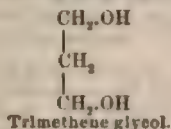
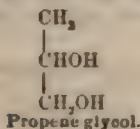
It is a liquid smelling like alcohol, having a specific gravity of 0.821 at 22°C . (71.6°F .), boiling at 104°C . (219.2°F .). With *chlorine* it gives mono-, di-, and trichloroacetal.

Ethidene-sulphonic acids.—The relation of these somewhat unstable acids to their isomerides, the ethene-sulphonic acids, is shown by the following formulae :—



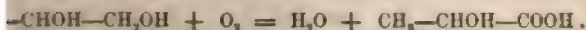
propene-disulphonic acid, $\text{CH}_3\text{CH}(\text{SO}_3\text{H})_2$, and *Ethidene-chlorosulphonic acid*, $\text{CH}_2=\text{CHSO}_3\text{H}$, are formed by heating ethidene dichloride (p. 518) with an aqueous solution of neutral sodium sulphite to about 140°C . (284°F .). The former is very unstable; the latter is moderately stable, and forms crystallized salts: its sodium salt crystallizes in nacreous laminae.

Propene Glycols, $\text{C}_3\text{H}_8\text{O}_2 = \text{C}_3\text{H}_7(\text{OH})_2$.—There are two of these alcohols, represented by the following formulæ:—



Propene glycol is analogous to the second and fourth modifications of the diatomic derivatives of propene, already described (p. 518). Glycols analogous to the first and third of these derivatives, viz., $\text{CH}_3-\text{CH}_2-\text{CX}_2$ and $\text{CH}_2=\text{CHX}$, are not known, and probably cannot exist, since it is already noticed, that two hydroxyl groups cannot be attached to the same atom.

Propene glycol is formed by heating the corresponding bromide, $\text{Br}-\text{CH}_2\text{Br}$, with silver acetate, and the resulting acetic ether is then distilled; also by heating propene chloride with water and lead oxide. It is a colorless oily liquid, having a sweet taste, a specific gravity of 0.859 at 0° , and boiling at $188^\circ-189^\circ\text{C}$. ($370.4^\circ-372.2^\circ\text{F}$.). In contact with potassium black it is oxidized to lactic acid:—



Heated to 100° with strong hydriodic acid, it gives pseudopropyl iodide, $\text{I}-\text{CH}_2\text{CH}_2\text{I}$. Phosphorus pentachloride converts it into propene chloride, $\text{CH}_3-\text{CHCl}-\text{CH}_2\text{Cl}$.

Propene chlorhydrin, $\text{CH}_3-\text{CHOH}-\text{CH}_2\text{Cl}$, is formed by the action of hydrogen chloride on the glycol, and by that of hypochlorous acid on propene. It has a specific gravity of 1.302 at 0° , and boils at 260.6°F .).

The corresponding *bromhydrin* boils at about 146°C . (294.8°F .).

Propene oxide, $\text{CH}_3-\text{CH}(\text{O})-\text{CH}_2$, formed by the action of aqueous potassium hypochlorhydrin, is a volatile liquid, boiling at 35°C . (95°F .), with a specific gravity of 0.859 at 0° , easily soluble in water. Nascent hydrogen converts it into secondary propyl alcohol, $\text{CH}_3-\text{CHOH}-\text{CH}_2$.

Trimethylene glycol, prepared from trimethylene bromide (p. 519), is a colorless liquid, boiling at 212°C . (413.6°F .).

Butene Glycols, $\text{C}_4\text{H}_{10}\text{O}_2 = \text{C}_4\text{H}_9(\text{OH})_2$.—Six of these compounds are theoretically possible, four derived from normal butane, and two from isobutane. Only two of them, however, are at present known, viz:—*1,2-Butene glycol*, $\text{CH}_3-\text{CHOH}-\text{CH}_2-\text{CH}_2\text{OH}$, is formed in small quantity by the action of sodium amalgam on acetic aldehyde in aqueous

TRIATOMIC ALCOHOLS AND ETHERS.

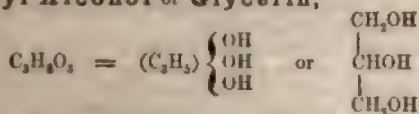
enic alcohols may be derived from saturated hydrocarbons by substitution of three atoms of hydroxyl for three atoms of hydrogen, and may be regarded as compounds of trivalent alcohol-radicles with atoms of hydroxyl, or as compounds derived from a triple molecule of H_2O , by substitution of a trivalent alcohol-radicle for three atoms of hydrogen. The hydrocarbons of the series $C_n H_{2n+2}$ should accordingly give rise to a series of triatomic alcohols of the form $(C_n H_{2n-1})(OH)_3$, viz. :—

| | | |
|------------------|-----------|----------------|
| ethenyl alcohol | | $CH(OH)_3$ |
| phenyl alcohol | | $C_6H_5(OH)_3$ |
| propenyl alcohol | | $C_3H_5(OH)_3$ |
| styrenyl alcohol | | $C_8H_7(OH)_3$ |
| pentenyl alcohol | | $C_5H_9(OH)_3$ |
| etc. | | etc. |

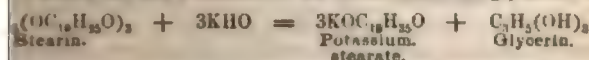
however, only two are known, viz., propenyl alcohol, or allyl alcohol, and pentenyl alcohol or amyl glycerin.

Triatomic alcohol subjected to the action of acids, or of the chlorides, or iodides of phosphorus, may yield three classes of ethers, from it by substitution of a halogen element, or acid radicle, for the whole of the hydroxyl; thus, from glycerin may be obtained hydrochloric ethers, $C_3H_5Cl(OH)_2$, $C_3H_5Cl_2(OH)$, $C_3H_5Cl_3$, and the iodic ethers, $C_3H_5(OC_2H_5O)(OH)_2$, $C_3H_5(OC_2H_5O)_2OH$, and $C_3H_5(OC_2H_5O)_3$.

Propenyl Alcohol or Glycerin,



This compound is obtained by the action of alkalis on natural fats, which, when saponified, the propenyl ethers of certain fatty acids; thus stearin, one of the constituents of mutton suet, consists of *propenyl tristearate*, $(C_3H_5O)_3(C_{18}H_{35}O)_3$, a compound derivable from glycerin itself, by substitution of $C_{18}H_{35}O$, for hydrogen. Now, when stearin is boiled with a caustic alkali, it is converted into a stearate of the alkali-metal and glycerin; thus:



The same reaction takes place when any other similarly constituted fat is saponified with a caustic alkali. The metallic salts of the fatty acids thus formed are the well-known bodies called soaps, and the process is called saponification; this term, originally restricted to actual soap-making, has been extended to all cases of the resolution of a compound ether into an alcohol, such, for example, as the conversion of ethyl acetate into acetic acid and ethyl alcohol by the action of alcoholic potash.

Propenyl alcohol was originally obtained by heating together olive or other oil, lead oxide, and water, as in the manufacture of common lead soap; an insoluble soap of lead is thereby formed, while the glycerin remains in the aqueous liquid. The latter is treated with sulphuretted hydrogen, digested with animal charcoal, filtered, and evaporated in a vacuum at the temperature of air. Glycerin is now produced in very large

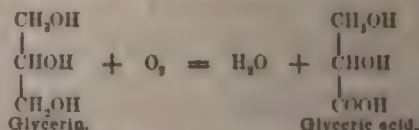
quantity and perfect purity in the decomposition of fatty substances by means of over-heated steam, a process which Mr. George Wilson has introduced into the manufacture of candles. In this reaction a fatty acid and glycerin are produced by assimilation of the elements of water: they are carried over by the excess of steam in a state of mechanical mixture, which rapidly separates into two layers in the receiver. The reaction is exactly similar to that which takes place when a caustic alkali is used to effect the saponification, *e. g.* :



Glycerin may also be produced from propenyl bromide, $(\text{C}_3\text{H}_5)\text{Br}$, a compound formed, as already observed, by the action of bromine on allyl iodide, $\text{C}_3\text{H}_5\text{I}$. The process consists in converting the propenyl bromide into propenyl triacetate, $(\text{C}_3\text{H}_5)(\text{OC}_2\text{H}_3\text{O})_3$, by the action of silver acetate and decomposing this ether with potash. This mode of formation must not, however, be regarded as an actual synthesis of glycerin from compounds of simpler constitution: for the allyl-compounds are themselves prepared from glycerin (p. 596).

Glycerin is a nearly colorless and very viscid liquid, of specific gravity 1.27, and boiling at 290°C . (554°F). When quite pure and anhydrous, it crystallizes on exposure to a very low temperature, especially if agitated, as in railway transport. The crystals are monoclinic, perfectly colorless and melt at 15.6°C . (60°F).^{*} Glycerin has an intensely sweet taste and mixes with water in all proportions: its solution does not undergo the alcoholic fermentation, but when mixed with yeast and kept in a warm place, it is gradually converted into propionic acid. Glycerin has no action on vegetable colors. Exposed to heat, it volatilizes in part, darkens, and decomposes, giving off, amongst other products, a substance called *acrolin*, $\text{C}_3\text{H}_4\text{O}$, having an intensely pungent odor.

Concentrated *nitric acid* converts glycerin into glyceric acid, $\text{C}_3\text{H}_5\text{O}_6$, an acid related to glycerin in the same manner as glycollic acid to glycol, and acetic acid to ethyl alcohol; being formed from it by substitution of oxygen for two atoms of hydrogen in immediate relation to hydroxyl, thus:



The formula of glycerin indicates the possibility of effecting a second substitution of the same kind, which would yield diglyceric acid, $\text{C}_3\text{H}_5\text{O}_7$, but this acid has not been actually obtained.

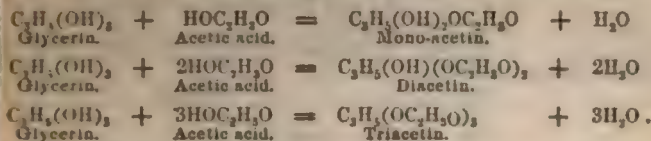
Glycerin, treated with a mixture of strong nitric and sulphuric acids, forms nitroglycerin, $\text{C}_3\text{H}_5(\text{NO}_2)_3\text{O}_3$, a heavy oily liquid which explodes powerfully by percussion. It is much used for blasting in mines and quarries, but is very dangerous to handle, and has given rise to several fatal accidents.

Glycerin combines with the elements of sulphuric acid, forming a sulphoglyceric acid, $\text{C}_3\text{H}_5\text{O}_3\text{SO}_3$, which gives soluble salts with lime, baryta, and lead oxide.

Monatomic *oxygen-acids* (acetic, benzoic, stearic, etc.), heated in sealed tubes with glycerin, yield compound ethers in which 1, 2, or 3 hydrogen-atoms of the glycerin are replaced by an equivalent quantity of the acid

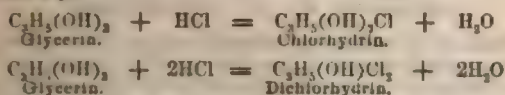
^{*} Rees, Chem. Soc. J. 1876, 1. 681.

Here, according to the proportions employed. The resulting compounds are denoted by names ending in *in*; thus:



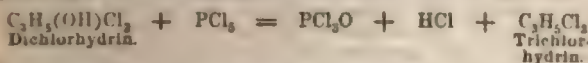
The glyceric ethers or glycerides thus produced are, for the most part, only liquids, increasing in viscosity as the acid from which they are produced has a higher molecular weight; those formed from the higher members of the fatty acid series, $\text{C}_{2n}\text{H}_{2n}\text{O}_2$ (such as palmitic and stearic acids), are solid fats. Some of the triacid glycerides, produced artificially the way just mentioned, are identical with natural fats occurring in the fats of plants and animals; thus tristearin is identical with the stearin of beef and mutton suet: triolein with the olein of olive oil, etc.

Hydrochloric and hydrobromic acids act upon glycerin in the same manner as oxygen-acids, excepting that the reaction always stops at the second stage. Just as in the action of these acids on the glycols it stops at the first stage. The ethers thus formed are called chlorhydrins, bromhydrins, etc., e. g.:



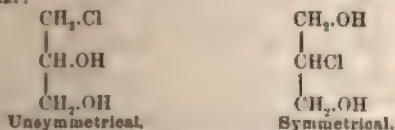
Hydroiodic acid acts somewhat differently, producing an ether, $\text{C}_6\text{H}_{11}\text{IO}$, which may be regarded as a double molecule of glycerin, having four equivalents of hydroxyl replaced by two atoms of oxygen, and a fifth by iodine, $\text{C}_6\text{H}_{10}\text{O}_2(\text{OH})\text{I}$.

The chlorides and bromides of phosphorus act upon glycerin in the same manner as hydrochloric and hydrobromic acid, but their action goes on to the third stage, producing trichlorhydrin, or propenyl chloride, and the corresponding bromine-compound:



Iodide of phosphorus acts on glycerin in a totally different manner, yielding isopropene or allyl iodide, $\text{C}_3\text{H}_5\text{I}$ (p. 596).

Monochlorhydrins, $\text{C}_3\text{H}_5\left\{\begin{smallmatrix} (\text{OH})_2 \\ \text{Cl} \end{smallmatrix}\right.$ —Of these compounds there are two isomeric forms, viz.:



The first is the chief product obtained by saturating glycerin with hydrochloric acid gas, and heating the liquid for some time over the water-bath. To purify it, the acid liquid is saturated with sodium carbonate, agitated with ether, the ethereal solution is evaporated, and the residual liquid subjected to fractional distillation.

Symmetrical dichlorhydrin is a thick liquid, easily soluble in the ether, and has a specific gravity of 1.44 at 15° C. (59° F.), boiling at 120–125° C. (248–255° F.), and is converted by sodium cyanide into propyl cyanide, $\text{CH}_3\text{CH}_2\text{CN}$.

Symmetrical dichlorhydrin is obtained by agitating allyl alcohol with aqueous hypochlorous acid:



It has a specific gravity of 1.44 at 15° C. (59° F.), and boils at 120–125° C. (248–255° F.).

Dichlorhydrin, $\text{C}_3\text{H}_6\text{Cl}_2$, $\left\{ \begin{array}{l} \text{CH}_2\text{Cl} \\ | \\ \text{CH} \\ | \\ \text{CH}_2\text{Cl} \end{array} \right.$ —It differs from the two isomeric

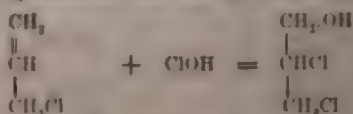
forms:



Both are formed by heating glycerin with strong hydrochloric acid for four, however, predominating. Thus, when in the contrary combination is best prepared by saturating a mixture of equal volumes of glycerin and glacial acetic acid with hydrochloric acid gas at 100° C., neutralizing the product with sodium carbonate, and subjecting it to fractional distillation. It may also be prepared by distilling glycerin with SOCl_2 . Lastly, it may be obtained quite pure by mixing epichlorhydrin, $\text{C}_3\text{H}_5\text{Cl}$, with fuming hydrochloric acid.

Symmetrical dichlorhydrin, or *dichlorinated propylglycol alcohol* is a liquid having an ethereal odor, a specific gravity of 1.44 at 15° C. (59° F.), boiling at 124° C. (255° F.), easily soluble in alcohol and sparingly in water. By *sodium cyanide* it is converted into propyl propyl alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, and by *oxidation* with dilute chromic acid mixture, into acetone dichloride, $\text{CH}_3\text{COClCH}_2\text{Cl}$. With *potassium cyanide* it forms dicyanhydrin, $\text{CH}_3\text{CNCH}_2\text{CH}_2\text{CN}$.

Unsymmetrical Dichlorhydrin (commonly called *chloride of allyl alcohol*) is formed by addition of chlorine to allyl alcohol, $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$, or of hypochlorous acid to allyl chloride:



It has a specific gravity of 1.375 at 0°; boils at 182–183° C. (359.6–361.4° F.), is converted by metallic sodium into allyl alcohol.

By the action of caustic potash or soda, both dichlorhydrins are converted, by abstraction of HCl , into epichlorhydrin.

Trichlorhydrin, *Glycerol trichloride*, or *Allyl trichloride*, $\text{C}_3\text{H}_2\text{Cl}_3$, $\left\{ \begin{array}{l} \text{CH}_2\text{Cl} \\ | \\ \text{CHCl} \\ | \\ \text{CHCl} \end{array} \right.$ is formed by the action of phosphorus pentachloride

on either of the dichlorhydrins; also (together with $\text{CH}_3\text{CHCl.CHCl}_2$) by the action of iodine chloride on propene chloride, $\text{CH}_3\text{CHCl.CH}_2\text{Cl}$; and by chlorination of propene and of pseudopropyl iodide. It is a liquid which smells like chloroform, has a specific gravity of 1.417 at 15°C . (59°F .), and boils at 158°C . (316.4°F .). Heated with solid potassium or sodium hydroxide, it forms dichloroglycide, $\text{CH}_2=\text{CCl}-\text{CH}_2\text{Cl}$, boiling at 94°C . (201.2°F .). Heated with sulphuric acid, it forms monochloracetone, $\text{CH}_3-\text{CO}-\text{CH}_2\text{Cl}$.

Bromhydrins. — *Monobromhydrin*, $\text{C}_3\text{H}_5(\text{OH})_2\text{Br} = \text{CH}_2\text{Br}-\text{CH}(\text{OH})-\text{CH}_2\text{OH}$, obtained by the action of hydrobromic acid on glycerin, is an oily liquid, boiling in a vacuum at 180°C . (356°F .).

Symmetrical Dibromhydrin, $\text{CH}_2\text{Br}-\text{CH}(\text{OH})-\text{CH}_2\text{Br}$, prepared from glycerin and hydrobromic acid, is a liquid having an ethereal odor, a specific gravity of 2.11 at 18°C . (64.4°F .), and boiling at 219°C . (426.2°F .). *Unsymmetrical dibromhydrin*, $\text{CH}_2\text{Br}-\text{CHBr}-\text{CH}_2\text{OH}$, from allyl alcohol and bromine, boils at $212-214^\circ\text{C}$. ($413.6-417.2^\circ\text{F}$.).

Tribromhydrin, *Glyceryl tribromide*, or *Allyl tribromide*, $\text{C}_3\text{H}_5\text{Br}_3 = \text{CH}_2\text{Br}-\text{CHBr}-\text{CH}_2\text{Br}$, is obtained by the action of bromine on allyl iodide:



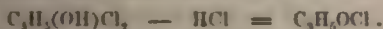
It crystallizes in colorless, shining prisms, melts at 16°C . (60.8°F .), boils at $219-220^\circ\text{C}$. ($426.2-428^\circ\text{F}$.); is converted by caustic potash or soda into dibromoglycide, $\text{CH}_2=\text{CBr}-\text{CH}_2\text{Br}$, boiling at $151^\circ-152^\circ\text{C}$. ($303.8-305.6^\circ\text{F}$.).

Iodhydrins. — *Monoiodhydrin*, $\text{C}_3\text{H}_5\left\{ \begin{array}{l} (\text{OH})_2 \\ \text{I} \end{array} \right.$, obtained by heating glycerin to 100°C . with hydriodic acid, is a viscid liquid, having a specific gravity of 1.783.

Di-iodhydrin, $\text{C}_3\text{H}_5(\text{OH})\text{I}_2 = \text{CH}_2\text{I}-\text{CH}(\text{OH})-\text{CH}_2\text{I}$, obtained by heating symmetrical dichlorhydrin with aqueous potassium iodide, is a thick oil, having a specific gravity of 2.4, and solidifying to a crystalline mass at -15°C . (5°F .).

Tri-iodhydrin or *Glyceryl tri-iodide*, $\text{C}_3\text{H}_5\text{I}_3$, does not appear to be capable of existing, inasmuch as the action of hydriodic acid, or of iodine and phosphorus on glycerin yields nothing but allyl iodide and free iodine.

Glycidic compounds. — When dichlorhydrin is treated with potash, it gives up a molecule of hydrochloric acid, and is converted into a compound, $\text{C}_3\text{H}_5\text{OCl}$, called *epichlorhydrin*:



This compound may be regarded as the hydrochloric ether of an alcohol, $\text{C}_3\text{H}_5\text{O}(\text{OH})$, called *glycide*, formed from glycerin by abstraction of H_2O . Dibromhydrin, $\text{C}_3\text{H}_5(\text{OH})\text{Br}_2$, treated in the same manner, yields *epibromhydrin*, or the hydrobromic ether of glycide, $\text{C}_3\text{H}_5\text{OBr}$. Epichlorhydrin heated with dry potassium iodide is converted into *epi-iodhydrin*, $\text{C}_3\text{H}_5\text{OI}$:



These glycidic ethers are easily reconverted into bodies of the glycerin

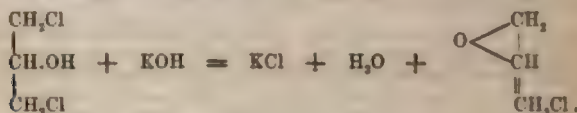
type. Thus epichlorhydrin combines with acetic acid, forming glyceric acetochlorhydrin:



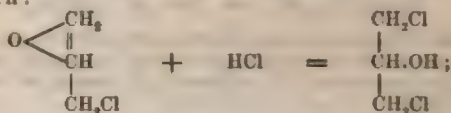
and with alcohol in like manner, forming glyceric ethylchlorhydrin, $(C_2H_5)Cl(OH)(OC_2H_5)$.

Epichlorhydrin unites directly with water, forming glyceric monochlorhydrin, $C_2H_5(OH)_2Cl$.

Epichlorhydrin or *Glycidic Hydrochloride*, isomeric with monochloracetone, may be obtained by agitating either of the dichlorhydrins with strong potash-lye:



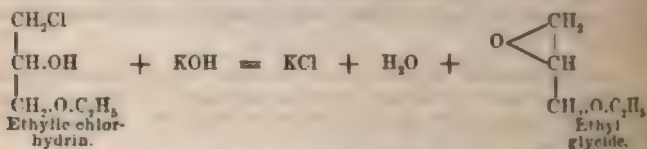
It is a mobile liquid, having a specific gravity of 1.194 at 0° , boiling at $119^\circ C.$ ($246.2^\circ F.$); insoluble in water; easily soluble in alcohol and ether. It smells like chloroform, and has a burning sweetish taste. When heated with fuming hydrochloric acid, it is converted into asymmetrical dichlorhydrin:



and by prolonged heating with water, into monochlorhydrin. Heated

with alcohols, it yields ethers of chlorhydrin, such as $C_2H_5 \begin{Bmatrix} Cl \\ OH \\ O.C_2H_5 \end{Bmatrix}$,

which, when distilled with potassium hydroxide, are converted into alcoholic glycides or glycidic ethers; thus:

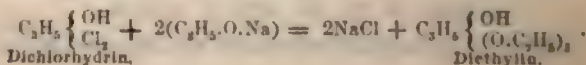


Ethyl-glycidic ether, $C_2H_5.O.C_2H_5$ (or *epiethylin*), boils at $126^\circ-130^\circ C.$ ($258.8^\circ F.$); *amyl-glycidic ether*, $C_2H_5.O.O.C_5H_{11}$, at $188^\circ C.$ ($370.4^\circ F.$).

Epibromhydrin, $C_2H_5.OBr$, from either of the two bromhydrins, boils at $139^\circ-140^\circ C.$ ($282.2^\circ-284^\circ F.$); *epi-iodhydrin*, $C_2H_5.OI$, obtained by heating epichlorhydrin with solution of potassium iodide, boils at about $160^\circ C.$ ($320^\circ F.$).

Trichlorhydrin, heated with potassium hydroxide, which abstracts HCl , yields dichloroglycidic ether, $C_2H_4Cl_2 = CH_2-CCl-CH_2Cl$.

Alcoholic Ethers of Glycerin.—Derivatives of glycerin containing alcohol-radicles are formed by heating the mono- and dichlorhydrins with sodium alcohol, thus:—



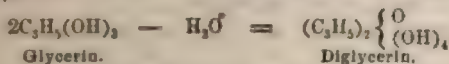
Mono-ethylin, $C_2H_5 \left\{ \begin{smallmatrix} (OH)_2 \\ OC_2H_5 \end{smallmatrix} \right.$, is soluble in water, and boils at $230^\circ C.$ ($446^\circ F.$). **Diethylin** is sparingly soluble in water, smells like peppermint, has a specific gravity of 0.92, and boils at $191^\circ C.$ ($375.8^\circ F.$). **Triethylin**, $C_2H_5(O.C_2H_5)_2$, formed by the action of ethyl iodide on the sodium-derivative of diethylin, is a liquid insoluble in water, boiling at $85^\circ C.$ ($365^\circ F.$).

Allylin, $C_3H_7 \left\{ \begin{smallmatrix} (OH)_2 \\ O.C_3H_7 \end{smallmatrix} \right.$, is produced by heating glycerin with oxalic acid, and occurs (together with glyceric oxide) in the residue left after heating the product to $260^\circ C.$ ($500^\circ F.$). It is a viscid liquid, boiling at $25^\circ-240^\circ C.$ ($437^\circ-464^\circ F.$).

Glyceric oxide or glycerin ether, $(C_3H_7)_2O_2$, occurring together with allylin, as just mentioned, boils at $169^\circ-172^\circ C.$ ($336.2^\circ-341.6^\circ F.$).

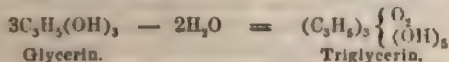
The ethers of glycerin containing acid radicles, including the natural oils and fats, will be described under the respective acids.

Polyglycerins.—Two, three, or more molecules of glycerin can unite to a single molecule, with elimination of a number of water-molecules—more by one than the number of glycerin molecules which combine together; thus:—



Glycerin.

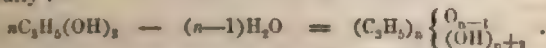
Diglycerin.



Glycerin.

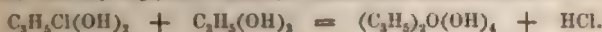
Triglycerin.

Generally:—



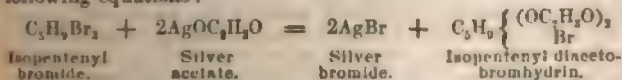
The product is a polyglycerin whose atomicity (determined by the number of equivalents of hydroxyl contained in it) is $n+2$.

The mode of preparing the polyglycerins is similar to that of the polybenic alcohols (p. 603), and consists in heating glycerin with monochlorhydrin, whereby diglycerin and hydrochloric acid are formed:—



The hydrochloric acid thus formed converts a fresh quantity of glycerin to chlorhydrin, which then acts in a similar manner on the diglycerin, and converts it into triglycerin; and in this manner the process is continued. The polyglycerins may then be separated by fractional distillation. Their properties are but little known.

Isopentenyl Alcohol, or Amyl Glycerin, $C_5H_{11}O_3 = (C_5H_9)(OH)_3$. This compound is formed from bromo-isopentene dibromide, $C_5H_9Br.Br_2$, isopentenyl bromide, C_5H_9Br , by the series of processes represented in the following equations:—

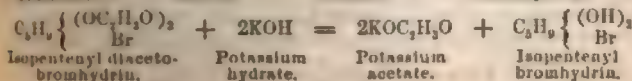


Isopentenyl bromide.

Silver acetate.

Silver bromide.

Isopentenyl diacetobromhydrin.

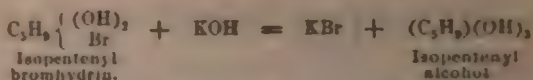


Isopentenyl diacetobromhydrin.

Potassium hydrate.

Potassium acetate.

Isopentenyl bromhydrin.



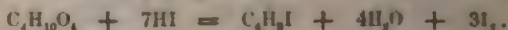
Amyl glycerin is a thick colorless liquid, having a sweet aromatic taste, and soluble in water.

TETRATOMIC ALCOHOLS AND ETHERS.

The only tetratomic alcohol at present known is :

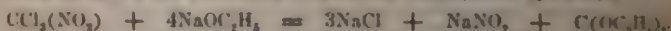
Erythrite, $\text{C}_4\text{H}_{10}\text{O}_4 = (\text{C}_2\text{H}_5)_2(\text{OH})_2$, also called *Erythromannite*, *Erythroglucin*, and *Phycite*, which is the tetratomic alcohol analogous to butyl alcohol, $\text{C}_4\text{H}_{10}\text{O}$, and butyl glycol, $\text{C}_4\text{H}_{10}\text{O}_2$; the corresponding glycerin is not known.

Erythrite is a saccharine substance, existing ready formed in *Hydrogonium vulgaria*. It was originally discovered by Dr. Stenhouse among the products of decomposition of erythric acid.* It crystallizes in large transparent prisms, is readily soluble in water, sparingly soluble in alcohol, insoluble in ether : not fermentable. Heated with *hydriodic acid*, it yields secondary butyl iodide, $\text{C}_4\text{H}_9\text{I}$ (p. 582):—



Heated with *oxygen acids*, it forms compound ethers, in the manner of alcohols in general; thus, with *benzoic acid*, $\text{C}_6\text{H}_5\text{O}_2$, or HOC_6H_5 , it forms a dibenzoate, $(\text{C}_6\text{H}_5)_2(\text{OH})_2(\text{OC}_6\text{H}_5)_2$, and a hexbenzoate, $(\text{C}_6\text{H}_5)_6(\text{OC}_6\text{H}_5)_2$, $2\text{C}_6\text{H}_5\text{O}_2$, consisting of neutral benzoyl-erythrite, united with two molecules of benzoic acid.

A tetratomic ether, viz., **Ethylie Orthocarbonate** or **Orthocarbonic Ether**, $\text{C}(\text{OC}_2\text{H}_5)_4$, analogous to carbon tetrachloride, CCl_4 , is formed by the action of sodium ethylate on chloropierin (p. 526) :



It is a liquid having an ethereal odor, and boiling at 158°C .– 159°C . (316.4–318.2° F.). Heated with ammonia, it yields guanidine, CN_2H_4 , and ethyl alcohol :



The corresponding alcohol, $\text{C}(\text{OH})_4$, has probably no existence, as much as one carbon-atom appears to be incapable of linking together two or more hydroxyl groups.

HEXATOMIC ALCOHOLS AND ETHERS.

This class of compounds includes most of the saccharine substances found in plants, and others produced from them by artificial transformation. Three of the natural sugars, mannite, dulcette, and sorbitol, having the composition $\text{C}_6\text{H}_{14}\text{O}_6$, or $\text{C}_2\text{H}_5(\text{OH})_2$, are saturated hexatomic alcohols derived from the saturated hydrocarbon, C_6H_{14} . Several others, called *glucoses*, contain $\text{C}_6\text{H}_{12}\text{O}_6$, that is to say, two atoms of hydrogen

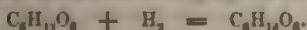
* See the Chapter on Coloring Matters.

less than mannite and dulcitol, and may therefore be regarded—so far as composition is concerned—as the aldehydes of these alcohols; moreover, ordinary glucose (grape-sugar) is converted into mannite by the action of nascent hydrogen, just as acetic aldehyde, C_2H_4O , is converted into common alcohol, C_2H_6O . Further, there are diglucosic alcohols, or saccharoses, $C_{12}H_{22}O_{11}(=2C_6H_{12}O_6-H_2O)$, related to glucoses in the same manner as diethenic alcohol to glycol, or diglycerin to glycerin: the most important of these are cane-sugar and milk-sugar; and, lastly, there are certain vegetable products called amyloses—viz., starch, cellulose, and a few others, represented by the formula $C_6H_{10}O_5$, or multiples thereof, which may be regarded as the oxygen-ethers or anhydrides of the glucoses, or of the diglucosic alcohols, inasmuch as they differ therefrom by a molecule of water.

These three groups of compounds, which consist of carbon united with hydrogen and oxygen in the proportion to form water, are included under the general name of carbohydrates.

Saturated Hexatomic Alcohols.

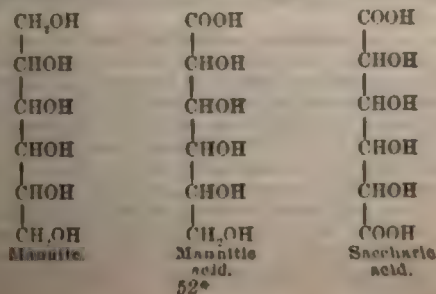
Mannite, $C_6H_{14}O_6=(C_6H_5)(OH)_6$.—This is the chief component of *mannu*, an exudation from a species of ash; it is also found in the juice of certain other plants, in several sea-weeds, and in mushrooms. It is best prepared by treating manna with boiling alcohol, and filtering the solution whilst hot; it then crystallizes on cooling in tufts of slender needles. Mannite may be produced artificially by treating a solution of glucose with sodium-amalgam, the glucose then taking up 2 atoms of hydrogen:



The same transformation of glucose sometimes takes place under the action of certain ferments.

Mannite crystallizes in thin four-sided prisms, easily soluble in water and in hot alcohol, insoluble in ether. It is slightly sweet, melts at $166^\circ C.$ ($330.8^\circ F.$), has no action on polarized light, and is not fermentable, except under very unusual conditions.

By oxidation in contact with *platinum black*, mannite is converted into mannitic acid, $C_6H_{12}O_7$, and mannitose, $C_6H_{12}O_6$, a kind of sugar isomeric with glucose. By oxidation with *nitric acid* it yields saccharic acid, $C_6H_{10}O_8$, and ultimately oxalic acid. Mannitic acid and saccharic acid are related to mannite in the same manner as glycollic acid and oxalic acid to glycol; the relation between the three compounds is shown by the following formulæ:

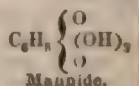
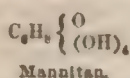


manner in alcohols in general, the elements of the mannites are uniting together, with elimination of one or more molecules of water, resulting compounds, called mannitanides, bear a considerable resemblance to the fats; but their composition has not been very determined.

These ethers, when saponified with alkalis, yield, not mannitan, $C_6H_{12}O_6$, a compound differing from mannite by one molecule of water. The same compound is obtained in small quantity by heating mannite to $200^{\circ} C.$ ($392^{\circ} F.$), and more easily by prolonged heating of mannite with strong hydrochloric acid. It is a syrupy liquid, which volatilizes slowly at $140^{\circ} C.$ ($284^{\circ} F.$), and dissolves easily in water and cold absolute alcohol: this last property affords the means of separating it from mannite. When exposed to the air, it slowly absorbs water and is reconverted into mannite; the change is accelerated by boiling with acids or with alkalis.

Mannite, boiled with *butyric acid*, gives up two molecules of water and is converted into mannide, $C_6H_{10}O_4$, which is also a syrupy liquid, but differs from mannitan in being much more volatile, evaporating at $140^{\circ} C.$ ($284^{\circ} F.$), and in being quickly reconverted into mannite by exposure to moist air. It dissolves easily in water, and in absolute alcohol.

The two anhydrides of mannite may be represented by the following formulae:—



Dulcite, $C_6H_{12}O_6$, also called *Dulcin*, *Dulcose*, and *Melampyr sugar*, isomeric with mannite, is obtained from a crystalline substance of unknown origin, imported from Madagascar: it is extracted there by boiling with water, and crystallizes from the filtered solution. It is likewise obtained from *Melampyrum nemorosum*, by mixing the decoction of the plant with lime, concentrating, adding hydrochloric acid in slight excess, and evaporating a little: it then separates in crystals when the liquid cools.

Isodulcite, $C_6H_{14}O_6$, or $C_6H_{12}O_5 \cdot H_2O$, a saccharine substance isomeric with mannite and dulcite, is produced by the action of dilute acids on quercitrin, a yellow substance occurring in quercitron bark. It forms large transparent, regularly developed crystals, resembling those of cane-sugar: it is sweeter than grape-sugar, not fermentable, dissolves in 2.09 parts of water at $18^\circ C.$ ($64.4^\circ F.$), and easily in absolute alcohol. The rotations turn the plane of polarization to the right. Isodulcite melts, with loss of water, between $105^\circ C.$ ($221^\circ F.$) and $110^\circ C.$ ($230^\circ F.$), is colored yellow or brown by strong sulphuric acid and caustic alkalis, and reduces cupric oxide. By a mixture of nitric and sulphuric acids, it is converted into a slightly explosive nitro-compound, $C_6H_5(NO_2)_3O_6$.

Sorbite, $C_6H_{14}O_6 + \frac{1}{2}H_2O$, occurs in the berries of the mountain-ash in small crystals, easily soluble in water. It gives off its water when heated, and melts at $110^\circ C.$ ($230^\circ F.$).

Mannite, dulcite, and sorbite are distinguished from the true sugars (sucoses and saccharoses) by not fermenting in contact with yeast, and not reducing an alkaline solution of cupric oxide.

Pinite and **Quercite** are naturally occurring saccharine bodies, isomeric with mannitan and dulcitan.

Pinite is contained in the sap of a Californian pine (*Pinus Lambertiana*), and is deposited from the aqueous extract of the hardened juice, in hard white crystalline nodules, as sweet as cane-sugar, very soluble in water, nearly insoluble in alcohol. It turns the plane of polarization of a luminous ray to the right; it is not fermentable. With benzoic acid, it forms

benzopinite, $C_6H_8 \left\{ \begin{array}{c} (OC_7H_5O)_3 \\ (OH)_1 \end{array} \right.$, and **tetrabenzopinite**,

$C_6H_8 \left\{ \begin{array}{c} (OC_7H_5O)_4 \end{array} \right.$; and similar compounds with stearic acid.

Quercite is a saccharine substance extracted from acorns, by treating the aqueous infusion with milk of lime to remove tannic acid, leaving the liquid to ferment with yeast to remove fermentable sugar, evaporating the residue to a syrup, and leaving it to crystallize. It forms hard monoclinic crystals, which grate between the teeth, and are soluble in water and in dilute alcohol. Heated in a sealed tube with benzoic acid, it forms **benzoquercite**, having the same composition as dibenzopinite.

CARBOHYDRATES.

This name, as already observed, is given to a class of compounds containing 6 or 12 atoms of carbon united with hydrogen and oxygen in the proportion to form water. They may be regarded as derivatives of the hexatomic alcohol, $C_6H_{14}O_6$, and are divided into the three following groups:—

| <i>Glucoses,</i>
$C_6H_{12}O_6$. | <i>Saccharoses,</i>
$C_{12}H_{22}O_{11}$. | <i>Amyloses,</i>
$C_6H_{10}O_5$. |
|--------------------------------------|---|--------------------------------------|
| + Grape-sugar*
or Dextrose. | + Cane-sugar
or Saccharose. | + Starch. |
| — Fruit-sugar
or Levulose. | + Parasaccharose. | + Dextrin. |
| Mannitose. | + Melitose. | + Glycogen. |
| + Galactose. | + Melezitose. | — Inulin. |
| Inosite. | + Trehalose. | Cellulose. |
| Sorbin. | + Mycose. | Tunicin. |
| + Eucalyn. | Symnathrose. | Gum. |
| Dambose. | + Milk-sugar
or Lactose. | |
| | + Maltose. | |

Most of these compounds occur in the vegetable organism; a few also, as dextrose, lactose, glycogen, and inosite, in the animal organism.

Glucoses, $C_6H_{12}O_6$.

The sugars included in this formula may be regarded as aldehydes, the saturated alcohols, $C_6H_{14}O_6$. Ordinary glucose (grape-sugar) is converted into mannite by the action of nascent hydrogen (p. 617), and, on the other hand, mannite, when slowly oxidized in contact with platinum black, is partly converted into mannitose. Nevertheless, the glucoses still exhibit the characteristic property of alcohols, namely, that of forming ethers by combination with acids and elimination of water. The formula of a glucose may indeed be derived from that of mannite given on page 617, by removing two hydrogen-atoms from one of the groups, CH_2OH , the other groups remaining as before: the glucoses may therefore be expected to act as pentatomic alcohols. Bodies thus constituted may be called *alcoholic aldehydes*.

The following varieties of glucose are known:—

1. *Ordinary glucose*, produced by hydration of starch under the influence of dilute acids or of diastase, and existing ready-formed, together with other kinds of sugar, in honey and various fruits, especially in grapes, and alone in diabetic urine.
2. *Levulose*, existing in cane-sugar which has been acted upon by acids and obtained pure by the action of dilute acids upon a variety of starch called inulin.
3. *Mannitose*, produced by oxidation of mannite.
4. *Galactose*, formed by the action of acids on milk-sugar.
5. *Inosite*, existing in muscular flesh.
6. *Sorbin*, obtained from mountain-ash berries.
7. *Eucalyn*, existing, together with another kind of sugar, in the so-called Australian manna.
8. *Dambose*, obtained from a saccharine substance existing in *Africa caoutchouc*.

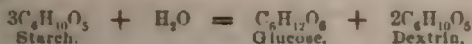
The first three of these glucoses exhibit but very slight differences in their chemical properties, differing chiefly indeed in their action on polarized light, and a few other physical properties. They all yield *osazones* on acid by oxidation. Galactose differs from them in yielding *mucic acid* when oxidized. Inosite, sorbin, and eucalyn exhibit still greater differences in their chemical properties, especially in not being fermentable except under very peculiar circumstances, whereas the four other glucoses

* The + sign indicates that the substance turns the plane of polarization to the right; the — sign indicates rotation to the left.

undergo vinous fermentation when placed, under certain conditions, in contact with yeast.

All the glucoses, except inosite, are decomposed by boiling with aqueous alkalis; this property distinguishes them from mannite and dulcite. They are not carbonized by strong sulphuric acid at ordinary temperatures. When boiled with a solution of potassio-cupric tartrate, they throw down the copper in the form of red cuprous oxide.

1. Ordinary Glucose, Dextro-glucose, Dextrose, $C_6H_{12}O_6$.—This variety of sugar is very abundantly diffused through the vegetable kingdom: it may be extracted in large quantity from the juice of sweet grapes (whence it is often called *grape-sugar*), also from honey, of which it forms the solid crystalline portion, by washing with cold alcohol, which dissolves the fluid syrup. The appearance of this substance, to an enormous extent, in the urine, is the most characteristic feature of the disease called *diabetes*. It exists in diabetic urine unmixed with any other kind of sugar, and is easily obtained by concentrating the liquid till it crystallizes, washing the crystals with cold alcohol, dissolving them in water, and re-crystallizing. It may also be prepared from starch by the action of diastase, a peculiar ferment existing in germinating barley, or by boiling with dilute sulphuric acid. In these reactions the starch takes up the elements of water, and is resolved into glucose and dextrin, a compound isomeric with starch itself.



Glucose, when required in considerable quantity, is always prepared from starch. Cellulose is likewise converted into glucose by the action of acids. Lastly, glucose is produced by boiling natural glucosides with dilute acids.

Glucose is much less sweet than cane-sugar, and less soluble in water and in alcohol; anhydrous glucose dissolves in 1.224 parts of water at $15^\circ C.$ ($59^\circ F.$). From its aqueous solution it separates in granular warty masses, consisting of a hydrate, $C_6H_{12}O_6 \cdot H_2O$, which leaves anhydrous glucose as a fused transparent mass when heated to $100^\circ C.$ ($212^\circ F.$), or as a dry white powder when heated to $55^\circ C.$ ($131^\circ F.$) or $60^\circ C.$ ($140^\circ F.$) in a stream of dry air. The alcoholic solution deposits anhydrous glucose in microscopic needles which melt at $140^\circ C.$ ($284^\circ F.$). In the state of solution glucose turns the plane of polarization of a ray of light to the right (hence the names *dextroglucose* and *dextrose*): its specific or molecular rotatory power is $+56^\circ$, and does not vary with the temperature (pp. 490-1).

Glucose may be heated to $120^\circ C.$ ($248^\circ F.$) or even $130^\circ C.$ ($266^\circ F.$) without alteration, but at $170^\circ C.$ ($338^\circ F.$) it gives off water, and is converted into glucosan, $C_6H_{10}O_5$, which, when freed from caramel (p. 626) by means of charcoal, and from glucose by fermentation, forms a colorless mass, scarcely sweet to the taste, and having somewhat less dextro-rotatory power than glucose. At higher temperatures glucose blackens and suffers complete decomposition. Glucose, boiled for some time with dilute sulphuric or hydrochloric acid, is converted into brown substances called alumin, ulmic acid, etc.—Strong sulphuric acid converts it at ordinary temperatures into sulpho-saccharic acid, $C_6H_{12}O_5SO_3$, which forms a soluble barium salt.

Lime, barite, and lead oxide dissolve slowly in aqueous solution of glucose, and on adding alcohol to the liquid, compounds of these oxides with glucose are precipitated. The barium compound is said to contain $(C_6H_{12}O_6)_2(BaO)_2, 2H_2O$; the calcium compound $(C_6H_{12}O_6)_2(CaO)_2, 2H_2O$; the lead compound $(C_6H_{12}O_6)_2(PbO)_2, (OH)_2$. These compounds are, however, very

unstable, being decomposed at the heat of boiling water. Glucose also combines with sodium chloride, forming the compound ($C_6H_{12}O_6$).NaCl.H₂O.

Glucose, boiled with a cupric salt in presence of alkalis, mainly reduces the cupric oxide to cuprous oxide: by this character it is easily distinguished from cane-sugar.

When solutions of cane-sugar and glucose are mixed with two separate portions of solution of cupric sulphate, and caustic potash is added in excess to each, deep-blue liquids are obtained, which, on being heated, exhibit different characters: the one containing cane-sugar is at first but little altered; a small quantity of red powder falls after a time, but the liquid long retains its blue tint; with the glucose, on the other hand, the first application of heat throws down a copious greenish precipitate, which rapidly changes to scarlet, and eventually to dark-red cuprous oxide, leaving a nearly colorless solution. If only small quantities of material are available, a mixture of cupric sulphate and tartaric acid, to which an excess of potash has been added, may be used with advantage. This solution, called *potassio-cupric tartrate*, is an excellent test for distinguishing the two varieties of sugar, or discovering an admixture of glucose with cane-sugar.

Glucose mixed in dilute solution with yeast and exposed to a temperature of 21°-26° C. (69.8°-78.8° F.), easily undergoes vinous fermentation (p. 563).

2. Levulose, $C_6H_{12}O_6$.—This sugar, distinguished from dextrose by turning the plane of polarization to the left, occurs, together with dextrose in honey, in many fruits, and in other saccharine substances. The mixture of these two sugars in equivalent quantities constitutes fruit-sugar or invert sugar, which is itself levorotatory, because the specific rotatory power of levulose is, at ordinary temperatures, greater than that of dextrose.

Cane-sugar may be *inverted*, that is, transformed into a mixture of equal parts of dextrose and levulose, by warming with dilute acids:



The same change is brought about by contact with yeast, or with *pepsin*, the peculiar ferment of fruits; it likewise takes place slowly when a solution of cane-sugar is left to itself.

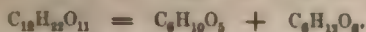
To separate the levulose, the invert sugar obtained from 10 grams of cane-sugar is mixed with 6 grams of slaked lime and 100 grams of water, whereby a solid calcium-compound of levulose is formed, while the rest of the dextrose remains in solution, and may be separated from the precipitate by pressure. The calcium salt of levulose, suspended in water and decomposed by carbon dioxide, yields a solution of pure levulose, which may be filtered and concentrated by evaporation. Levulose may be at once obtained in the pure state by the action of dilute acids on molasses.

Levulose is a colorless, uncrystallizable syrup, as sweet as cane-sugar, more soluble in alcohol than dextrose. Its rotatory power is much greater than that of dextrose at ordinary temperatures, but diminishes as the temperature rises. For the transition tint between the blue and the purple $[\alpha] = -108^\circ$ at 14° C. (57.2° F.); $= -79.5^\circ$ at 52° C. (125° F.); $= -53^\circ$ at 90° C. (194° F.). Now, the rotatory power of dextrose is the same at all temperatures, and equal to $+56^\circ$, consequently that of invert sugar, which is -25° at 15° C. (59° F.), diminishes by about one-third at 52° C. (125° F.), becomes nothing at 90° C. (194° F.), and changes sign above that temperature.

Levulose exhibits, for the most part, the same chemical reactions as

dextrose, but is more easily altered by heat or by acids, and on the contrary offers greater resistance to the action of alkalis or of ferments.

Levulose, $C_6H_{10}O_5$, the oxygen-ether or anhydride of levulose, is produced, together with dextrose, by melting cane-sugar for some time at $160^\circ C.$ ($320^\circ F.$):



The dextrose may be removed from the liquid by fermentation, and the levulose, which is unfermentable, may be obtained by evaporation as an uncrystallizable syrup. By boiling with water or dilute acids, it is converted into a fermentable levorotatory sugar, probably levulose.

3. **Mannitose**, $C_6H_{12}O_6$.—This is the sugar produced, together with mannitic acid, by the oxidation of mannite in contact with platinum black. It may be separated by saturating the liquid with lime, precipitating the calcium mannitate with alcohol, evaporating the filtrate to a syrup, adding alcohol, again filtering, and evaporating to dryness.

Mannitose is syrupy, uncrystallizable, fermentable, inactive to polarized light, and resembles the other glucoses in its chemical reaction.

4. **Galactose**, $C_6H_{12}O_6$, is produced by boiling milk-sugar with dilute acids. It is soluble in water, sparingly soluble in cold alcohol, crystallizes more readily than ordinary glucose; has a dextro-rotatory power of $+83.3^\circ$, and is very easily fermentable. It resembles dextrose in most of its reactions, but is distinguished from all the four glucoses above described by yielding mucic instead of saccharic acid, when oxidized by nitric acid.

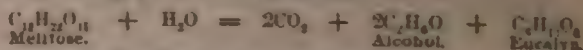
5. **Inosite**, or **Phaseomannite**, $C_6H_{12}O_6$, is a variety of glucose occurring in the muscular substance of the heart and other organs of the animal body; also in green kidney beans, the unripe fruit of *Phaseolus vulgaris*, and in many other plants. It forms prismatic crystals, resembling gypsum, soluble in water, but insoluble in alcohol and ether. It may be boiled with a strong aqueous potash or baryta without alteration or coloration. If this sugar be evaporated with nitric acid nearly to dryness, the residue mixed with a little ammonia and calcium chloride, and again evaporated, a beautiful and characteristic rose tint is produced.

Inosite does not ferment with yeast, but in contact with cheese, flesh, or decaying membrane and chalk, it undergoes lactic fermentation, producing lactic, butyric, and carbonic acids.

6. **Sorbin**, $C_6H_{12}O_6$, is a crystallizable sugar existing in the juice of ripe mountain-ash berries (*Sorbus aucuparia*). The juice when allowed to stand for some time in open vessels, deposits a brown crystalline matter, which may be obtained in transparent colorless crystals belonging to the trimetric system. This substance is almost insoluble in alcohol, but easily soluble in water, to which it imparts an exceedingly sweet taste. A solution of sorbin, mixed with ammonia and lead acetate, yields a white flocculent precipitate, containing $C_{12}H_{18}Pb_2O_{12}.PbO_2$. With sodium chloride it forms a compound which crystallizes in cubes.

Sorbin is converted by nitric acid into tartaric, racemic, and aposorbic acids. It does not ferment with yeast, but in contact with cheese and chalk, at $40^\circ C.$ ($104^\circ F.$), it undergoes lactic fermentation, yielding a large quantity of lactic acid, together with alcohol and butyric acid.

7. **Eucalyn**, $C_6H_{12}O_6$, is an unfermentable sugar, separated in the fermentation of melitose (the sugar of the *Eucalyptus* of Tasmania; in consequence of the destruction of a fermentable kind of sugar, which, in combination with eucalyn, constitutes melitose):



On evaporating the liquid, the eucalyn remains as an uncrystallizable syrup, having a specific rotatory power of $+165^\circ$ nearly. It is not rendered fermentable by the action of sulphuric acid.

8. **Dambosé**, $C_6H_{12}O_6$, obtained by heating dambonite with hydrotic acid, crystallizes in six-sided prisms, melting at $212^\circ C.$ ($413.6^\circ F.$)

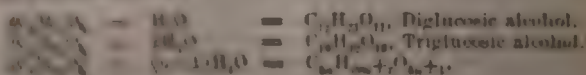
Dambonite, its methylic ether, $C_6H_{10}(CH_3)_2O_6$, occurs in a peculiar kind of caoutchouc from the *Galoon* in West Africa, from which it may be extracted by alcohol. It crystallizes from alcohol in six-sided prisms, dissolves easily in water, melts at $190^\circ C.$ ($374^\circ F.$), and sublimates at $285-210^\circ C.$ ($382-410^\circ F.$) in slender shining needles.

GLUCOSIDES.—When ordinary glucose is heated to $100^\circ-125^\circ C.$ ($212-248^\circ F.$) for fifty or sixty hours with acetic, butyric, stearic, benzoic and other organic acids, the two unite, with elimination of water, and compound ethers called glucosides are formed, analogous to the mannosides. A number of these artificial glucosides have been prepared by Berthelot, who regards them as derivatives of *glucosan*, $C_6H_{10}O_3$, because when heated with alkalis they yield glucosan, not glucose. Thus, there is a glucose-butyric ether to which Berthelot assigns the formula $C_6H_5(C_4H_7O_2)_2$, and an acetic ether, which he regards as hexa-aceto-glucosan, $C_6H_5(C_2H_3O_2)_6$, but they are merely oily liquids, which are very difficult to obtain pure and therefore their analyses are not much to be depended on.

A considerable number of bodies of similar constitution exist *nature* formed in plants, many of them constituting the bitter principles of the vegetable kingdom. None of these natural glucosides have been prepared artificially, but they are all resolved by boiling with dilute acids into glucose and some other compound. The most important of them will be described in a future chapter.

POLYGLUCOSIC ALCOHOLS.

The compounds of this group, including cane-sugar and other bodies, formed by the uniting of two or more molecules of glucose, with elimination of a number of molecules of water, may be more than the number of glucose molecules which compose the combination.



Among the natural alcohols of this class are diglucosic alcohols, $C_{12}H_{22}O_{11}$. Butyric, stearic, and other plant constituents, appear to be the most commonest independent, or poly-glucosic alcohols of higher orders.

Cane sugar or Macccharose, $C_{12}H_{22}O_{11}$.—This most useful substance is found in the stems of the grasses, in the sap of several

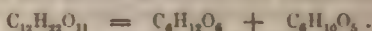
best trees, in the root of the beet and the mallow, and in several other plants. Most sweet fruits contain cane-sugar, together with invert sugar (p. 622); some, as walnuts, hazel-nuts, almonds, coffee-beans, and St. John's-bread (the fruit of *Ceratonia siliqua*), contain only cane-sugar. Honey and the nectars of flowers contain cane-sugar together with invert sugar; the sugar in the nectary of cactuses is almost wholly cane-sugar.

Sugar is extracted most easily and in greatest abundance from the sugarcane (*Saccharum officinarum*), cultivated for the purpose in many tropical countries. The canes are crushed between rollers, and the expressed juice is suffered to flow into a large vessel, where it is slowly heated nearly to its boiling point. A small quantity of slaked lime mixed with water is then added, which occasions the separation of a coagulum consisting chiefly of earthy phosphates, waxy matter, a peculiar albuminous principle, and mechanical impurities. The clear liquid separated from the coagulum is rapidly evaporated in open pans, heated by a strong fire made with the crushed canes of the preceding year, which have been dried in the sun, and preserved for the purpose. When sufficiently concentrated, the syrup is transferred to a shallow vessel, and left to crystallize, during which time it is frequently agitated in order to hasten the change and under the formation of large crystals. It is lastly drained from the dark non-crystallizable syrup, or *molasses*, and sent into commerce, under the name of *raw* or *Muscovado* sugar. The refining of this crude product is effected by redissolving it in water, adding a quantity of albumin in the shape of serum of blood or white of egg, and sometimes a little lime-water, and heating the whole to the boiling point: the albumin coagulates, and forms a kind of network of fibres, which inclose and separate from the fluid all mechanically suspended impurities. The solution is decolorized by filtration through animal charcoal, evaporated to the crystallizing point, and put into conical earthen moulds, where it solidifies, after some time, to a confusedly crystalline mass, which is drained, washed with a little clean syrup, and dried in a stove: the product is ordinary *loaf-sugar*. When the crystallization is allowed to take place quietly and slowly, *sugar candy* results, the crystals under these circumstances acquiring large volume and regular form. The evaporation of the decolorized syrup is not conducted in strong close boilers exhausted of air: the boiling point of the syrup is reduced in consequence from 110° C. (230° F.) to 65.50° C. (150° F.), or below, and the injurious action of the heat upon the sugar is in great measure prevented. Indeed, the production of molasses in the West Indian colonial manufacture is chiefly the result of the high and long-continued heat applied to the cane-juice, and might be almost entirely prevented by the use of vacuum-pans, the product of sugar being thereby greatly increased in quantity, and so far improved in quality as to become almost equal to the refined article.

In many parts of the continent of Europe, sugar is manufactured on a large scale from beet-root, which contains about 8 per cent. of that substance. The process is far more complicated and troublesome than that just described, and the raw product much inferior. When refined, however, it is scarcely to be distinguished from the preceding. In the Western States of America, sugar is prepared in considerable quantity from the sap of the sugar maple (*Acer saccharinum*), which is common in those parts. The tree is tapped in the spring by boring a hole a little way into the wood, and inserting a small spout to convey the liquid into a vessel placed for its reception. This is boiled down in an iron pot, and furnishes a *raw* sugar, which is almost wholly employed for domestic purposes, but is finding its way into commerce.

Pure sugar slowly separates from a strong solution in large, transparent colorless crystals, having the figure of a modified monoclinic prism. The crystals have a specific gravity of 1.6, and are unchangeable in the air. Sugar has a pure sweet taste, is very soluble in water, requiring for solution only one-third of its weight in the cold, and is also dissolved by alcohol, but less easily. When moderately heated it melts, and solidifies on cooling to a glassy amorphous mass, familiar as *barley-sugar*.

Cane-sugar, heated a little above 160°C . (320°F .), is converted, without loss of weight, into a mixture of dextrose and levulose (p. 623).



At a higher temperature, water is given off, the dextrose being probably converted into glucosan (p. 622): afterwards, at about 210°C . (410°F .), more water goes off, and a brown substance called caramel remains, consisting of a mixture of several compounds, all formed from sugar by elimination of water. At a still higher temperature, an inflammable gaseous mixture is given off, consisting of carbon monoxide, marsh-gas, and carbon dioxide; a distillate is obtained, consisting of brown oils, acetic acid, acetone, and aldehyde; and a considerable quantity of charcoal remains behind. The brown oils contain a small quantity of furfural, and a bitter substance called *assamar*.

By prolonged boiling with water, cane-sugar is converted into invert sugar. This transformation is accelerated by the presence of acids, and apparently also of certain salts. Different acids act with various degrees of rapidity—mineral more quickly than organic acids, sulphuric acid most quickly of all. By prolonged boiling even with very dilute acids, sugar is decomposed, yielding a number of brown amorphous products called ulmin, ulmic acid,* etc.; if the air has access to the liquid, formic acid is likewise produced. Concentrated hydrochloric acid decomposes sugar very quickly.

Strong sulphuric acid decomposes dry sugar when heated, and a concentrated solution, even at ordinary temperatures, with copious evolution of sulphurous oxide, and formation of a large quantity of black carbonaceous matter. By this reaction cane-sugar may be distinguished from glucose.

Cane-sugar is very easily oxidized. It reduces silver and mercury salts when heated with them, and precipitates gold from the chloride. Pure cupric hydrate is but slowly reduced by it, even at the boiling heat; in presence of alkali, however, a blue solution is formed, and on boiling the liquid, cuprous oxide is slowly precipitated (p. 622). Cane-sugar takes fire when triturated with 8 parts of lead dioxide, and fuses with potassium chlorate a mixture which detonates on percussion, and burns vividly when a drop of oil of vitriol is let fall upon it. Distilled with a mixture of sulphuric acid and manganese dioxide, it yields formic acid. Heated with dilute nitric acid, it yields saccharic and oxalic acids. 1 part sugar mixed with 3 parts nitric acid, of specific gravity 1.25 to 1.30, and heated to 50°C . (122°F .), is wholly converted into saccharic acid:



* Under the names *ulmin* and *ulmic acid* have been confounded a number of brown or black uncrystallizable substances produced by the action of powerful chemical agents upon sugar, lignin, etc., or generated by the putrefactive decay of vegetable fibre. Common garden mould, for example, treated with dilute, boiling solution of caustic potash, yields a deep-brown solution, from which acids precipitate a flocculent, brown substance, having but a slight degree of solubility in water. This is generally called *ulmic* or *humic acid*, and its origin is ascribed to the reaction of the alkali on the *ulmin* or *humus* of the soil. These bodies differ exceedingly in composition, and are too indefinite to admit of ready investigation.

At the boiling heat, the product consists chiefly of oxalic acid. Very strong nitric acid, or a mixture of strong nitric and sulphuric acids, converts sugar into nitrosaccharose, probably $C_{12}H_{18}(NO_2)_4O_{11}$. Sugar is likewise oxidized by chloride of lime, but the products have not been examined.

Cane-sugar does not turn brown when triturated with alkalis, a character by which it is distinguished from glucose: it combines with them, however, forming compounds called *sucrates*. By boiling with potash-lye it is decomposed, but much more slowly than the glucoses.

Potassium- and Sodium-compounds of cane-sugar, $C_{12}H_{22}KO_{11}$ and $C_{12}H_{21}NaO_{11}$, are formed, as gelatinous precipitates, on mixing an alcoholic solution of cane-sugar with potash- or soda-lye.

A *Barium-compound*, $C_{12}H_{20}BaO_{11}.H_2O$, or $C_{12}H_{17}O_{11}.BaO$, is obtained, as a crystalline precipitate, on adding hydrate or sulphide of barium to an aqueous solution of sugar. It may be crystallized from boiling water, but is insoluble in alcohol.

Calcium-compounds.—Lime dissolves in sugar-water much more rapidly than in pure water. The solution has a bitter taste, and is completely but slowly precipitated by carbonic acid. There are three or four of these compounds, which may be approximately represented by the following formulae:—

- | | |
|-----------------------------------|--------------------------------------|
| 1. $C_{12}H_{22}O_{11}.CaO$. | 3. $C_{12}H_{17}O_{11}.2CaO.2H_2O$. |
| 2. $2C_{12}H_{22}O_{11}.3CaO (?)$ | 4. $C_{12}H_{17}O_{11}.3CaO$. |

Magnesia and lead oxide are also dissolved by sugar-water. A crystalline lead-compound, $C_{12}H_{18}Pb_2O_{11}$, is precipitated on mixing sugar-water with neutral lead-acetate and ammoniac.

Sugar also forms crystalline compounds with *sodium chloride*.

Cane-sugar is not directly fermentable, but when its dilute aqueous solution is mixed with yeast, and exposed to a warm atmosphere, it is first resolved into a mixture of dextrose and levulose, which then enter into fermentation, yielding alcohol and carbon dioxide.

Parasaccharose, $C_{12}H_{22}O_{11}$.—This is an isomeride of cane-sugar, produced, according to Jodin,* by spontaneous fermentation. An aqueous solution of cane-sugar containing ammonium phosphate, left to itself for three months in summer, yielded, under circumstances not further specified, a crystalline sugar, isomeric with saccharose, together with an amorphous sugar having the composition of a glucose, both dextro-rotatory. Parasaccharose is very soluble in water, nearly insoluble in alcohol of 90 per cent. Its specific rotatory power at $100^\circ C.$ ($500^\circ F.$) = $+108^\circ$, appearing to increase a little with rise of temperature. It does not melt at 100° , but becomes colored, and appears to decompose. It reduces an alkaline cupric solution, but only half as strongly as dextro-glucose. It is but perceptibly altered by dilute sulphuric acid, even at $100^\circ C.$; hydrochloric acid weakens its rotatory power, turns the solution brown, and lightens its reducing power for cupric oxide.

Melitose, $C_{12}H_{22}O_{11}$.—A kind of sugar obtained from the manna which falls in copious drops from various species of *Eucalyptus* growing in Tasmania. It is extracted by water, and crystallizes in extremely thin interlaced needles, having a slightly saccharine taste.

The crystals of melitose are hydrated, containing $C_{12}H_{22}O_{11}.3H_2O$. They

* Comptes Rendus, III. 1252; liv 720.

give off 2 molecules of water at 100°C ., and become anhydrous at 130°C . (266°F .). They dissolve in 9 parts of cold water, very easily in boiling water, and dissolves also in boiling alcohol more freely than mannite. The alcoholic solution yields small but well-developed crystals. The aqueous solution turns the plane of polarization to the right: for the transition tint $[\alpha] = +102^{\circ}$.

Melitose, heated with dilute sulphuric acid, is resolved into a fermentable sugar (probably dextrose), and non-fermentable eucalyn (p. 624). Melitose ferments in contact with yeast, but is resolved, in the first instance, into glucose and eucalyn. It does not reduce an alkaline cupric solution, and is not altered by boiling with dilute alkalies or with barite-water. It is oxidized by nitric acid, yielding a certain quantity of mucic acid, together with a large quantity of oxalic acid.

Melezitose, $\text{C}_{11}\text{H}_{22}\text{O}_{11}$.—This variety of sugar is found in the so-called manna of Briangon, which exudes from the young shoots of the larch (*Larix europæa*). The manna is exhausted with alcohol, which, when evaporated, yields melezitose in very small, hard, shining, efflorescent crystals, which give off 4 per cent. of water when heated, and melt below 140°C . (284°F .) without further alteration, forming a liquid which solidifies to a glass on cooling. Melezitose is dextro-rotatory: $[\alpha] = +94.15$. It dissolves easily in water, is nearly insoluble in cold, slightly soluble in boiling alcohol.

Melezitose decomposes at about 200°C . (392°F .). It is carbonized by cold strong sulphuric acid, quickly turns brown with boiling hydrochloric acid, and forms oxalic acid with nitric acid. By an hour's boiling with dilute sulphuric acid, it is converted into glucose. In contact with yeast, it passes slowly, or sometimes not at all, into vinous fermentation. It is not altered at 100°C . by aqueous alkalies, and scarcely by potassio-cupric tartrate.

Trehalose, $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{H}_2\text{O}$, is obtained from *Trehala manna*, the produce of a species of *Echinops* growing in the East, by extraction with boiling alcohol. It forms shining rhombic crystals, containing $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{H}_2\text{O}$, which melt when quickly heated to 109°C . (228.2°F .); but it slowly heated give off their water even below 100° . It has a strongly saccharine taste, dissolves easily in water and in boiling alcohol, but is insoluble in ether. The aqueous solution is dextro-rotatory: $[\alpha] = +199^{\circ}$.

By several hours' boiling with dilute sulphuric acid, it is converted into dextrose. With strong nitric acid it forms a detonating nitro-compound. heated with dilute nitric acid it yields oxalic acid. In contact with yeast it passes slowly and imperfectly into alcoholic fermentation. It is not altered by boiling with alkalies, and does not reduce cuprous oxide from alkaline cupric solutions. Heated with acetic or butyric acid, it yields compounds not distinguishable from those which are formed in like manner from dextrose (p. 621).

Mycose, $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{H}_2\text{O}$, is a kind of sugar, very much like trehalose, obtained from ergot of rye by precipitating the aqueous extract of the fungus with basic lead acetate, removing the lead from the filtrate by sulphuric acid, evaporating to a syrup, and leaving the liquid to crystallize. It differs from trehalose only in possessing a somewhat feebler rotatory power: $[\alpha] = +192.5^{\circ}$, and in not being completely dehydrated at 100° .

Synanthrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, occurs in the tubers of *Dahlia variabilis*, of the Jerusalem artichoke (*Helianthus tuberosus*), and other plants of the com-

ite or synanthraceous order. It is a light amorphous powder, very deliquescent, not sweet, and without action on polarized light. It is resolved by dilute acids or by yeast into dextrose and levulose, and yields saccharic acid by oxidation.

Milk-sugar, Lactin, or Lactose. $C_{12}H_{22}O_{11} \cdot H_2O$.—This kind of sugar is an important constituent of milk: it is obtained in large quantities by evaporating *whey* to a syrupy state, and purifying the lactose, which slowly crystallizes out, with animal charcoal. It forms white, translucent, four-sided, trimetric prisms, of great hardness. It is slow and difficult of solution in cold water, requiring for that purpose five or six times its weight. Its specific rotatory power in aqueous solution is $[\alpha] = +58.30^\circ$. It has a faint, sweet taste, and in the solid state feels gritty between the teeth. When heated, it loses water, and at a high temperature blackens and decomposes. Milk-sugar combines with bases, forming compounds which have an alkaline reaction, and are easily decomposed. Dilute acids convert it into gалаctose (p. 613).

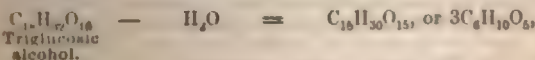
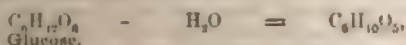
Milk-sugar, when distilled with oxidizing mixtures, such as sulphuric acid and manganese dioxide, yields formic acid. With nitric acid, it forms succinic, saccharic, tartaric, and a small quantity of racemic acid, and finally lactic acid. Very strong nitric acid, or a mixture of nitric and sulphuric acids, converts milk-sugar into a crystalline substitution-product called nitrolactin.

Milk-sugar is not brought immediately by yeast into the state of alcoholic fermentation; but when it is left for some time in contact with yeast, fermentation gradually sets in. When cheese or gluten is used as the ferment, the milk-sugar is converted into lactic acid. Alcohol is, however, always formed at the same time, especially if no chalk is added to neutralize the acid as it forms; the quantity of alcohol formed is greater also as the solution is more dilute.

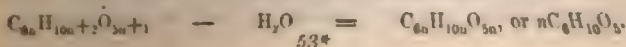
Maltose.—This is a sugar isomeric with lactose, produced by the action of malt-extract on starch. It is less soluble in alcohol than dextrose, has a reducing power about two-thirds as great as that of dextrose, and a specific rotatory power of $+56^\circ$. By the prolonged action of acids it is converted into dextrose.

OXYGEN-ETHERS OR ANHYDRIDES OF THE POLY-GLUCOSIC ALCOHOLS—
AMYLOSES.

These compounds, which are important constituents of the vegetable kingdom, may be derived from glucose and the poly-glucosic alcohols by abstraction of a molecule of water:



⋮

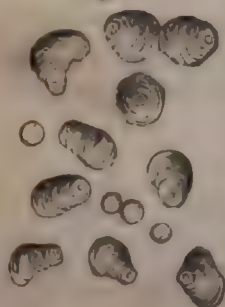


All these bodies are therefore isomeric or polymeric one with the other. Their compounds with metallic oxides, etc., have not been sufficiently investigated to fix their exact molecular weight, or to determine in each case the value of n ; but from the mode of conversion of starch into glucose and the constitution of certain substitution-products obtained by the action of nitric acid on cellulose, it appears most probable that in these bodies $n = 3$.

Starch. $nC_6H_{10}O_5$, probably $C_{18}H_{30}O_{15}$, also called *Fecula* and *Amidon*.—This is one of the most important and widely diffused of the vegetable proximate principles, being found to a greater or less extent in every plant. It is most abundant in certain roots and tubers, and in soft stems: some often contain it in large quantity. From these sources the starch is obtained by rasping or grinding the vegetable structures to pulp, and washing the mass upon a sieve, by which the torn cellular tissue is retained, while the starch passes through with the liquid, and eventually settles down from the latter, as a soft, white, insoluble powder, which may be washed with cold water, and dried at a very gentle heat. Potatoes treated in this manner yield a large proportion of starch. Starch from grain may be prepared in the same manner, by mixing the meal with water to a paste, and washing the mass upon a sieve: a nearly white insoluble substance called *gluten* is then left, containing a large proportion of nitrogen. The gluten of wheat flour is extremely tenacious and elastic. The value of meal as an article of food greatly depends upon this substance. Starch from grain is commonly manufactured on the large scale by steeping the material in water for a considerable time, when the lactic acid, which is developed under such circumstances from the sugar of the seed, dissolves, and in part dissolves the azotized matter, thereby greatly facilitating the mechanical separation of that which remains. A still more exact and

successful process has lately been introduced, in which a very dilute solution of caustic soda, containing about 200 grams of alkali to a gallon of liquid, is employed with the same view. Excellent starch is thus prepared from rice. Starch is insoluble in cold water, as indeed its mode of preparation sufficiently shows; it is equally insoluble in alcohol and other liquids, which do not effect its decomposition. To the naked eye it presents the appearance of a soft, white, and often glistening powder: under the microscope it is seen to be altogether destitute of crystalline structure, but to possess, on the contrary, a kind of organization, being made up of multitudes of little rounded transparent bodies, upon each of which a series of compressed parallel rings, surrounding a central spot or hilum, may often be traced. These starch

Fig. 174.



granules from different plants vary both in magnitude and form: those from the *Canna coccinea*, or *tour lez mois*, and potato being the largest, and those from wheat, and the cereals in general, very much smaller. Figure 174 represents granules of potato-starch, highly magnified.

When a mixture of starch and water is heated to near the boiling point of the latter, the granules burst and disappear, producing, if the proportion of starch is considerable, a thick gelatinous mass, very slightly opalescent, from the shreds of fine membrane, the envelope of each original granule. By the addition of a large quantity of water, this gelatinous starch, or *amidon*, may be so far diluted as to pass in great measure through

Blot-paper. It is very doubtful, however, how far the substance itself is really soluble in water, at least when cold; it is more likely to be merely suspended in the liquid in the form of a swollen, transparent, and insoluble jelly, of extreme tenuity. Gelatinous starch, exposed in a thin layer to a dry atmosphere, becomes converted into a yellowish, horny substance, like gum, which, when put into water, again softens and swells.

Thin gelatinous starch is precipitated by many of the metallic oxides, lime, baryta, and lead oxide; also by a large addition of alcohol. Infusion of galls throws down a copious yellowish precipitate containing tannic acid, which re-dissolves when the solution is heated. By far the most characteristic reaction, however, is that with free iodine, which forms with starch a deep indigo-blue compound, which appears to dissolve in free water, although it is insoluble in solutions containing free acid or lime matter. The color of the blue liquid is destroyed by heat, temporarily if the heat be quickly withdrawn, and permanently if the boiling is long continued, in which case the compound is decomposed, and the lime volatilized. Dry starch, put into iodine-water, acquires a purplish-ack color.

The unaltered and the gelatinous starch, when dry, have the same empirical formula, $C_6H_{10}O_5$. A compound of starch and lead oxide was found to contain, when dried at 100° , $C_6H_{10}O_5 \cdot PbO$, or $C_{12}H_{20}O_{10} \cdot 3PbO$.

Starch is an important article of food, especially when associated, as in ordinary meal, with albuminous substances. Arrow-root, and the fecula of the *Canna coccinea*, are very pure varieties, employed as articles of diet; arrowroot is obtained from the *Maranta arundinacea*, cultivated in the West Indies; it is with difficulty distinguished from potato-starch.—*Tapioca* is separated from the root of the *Jatropha Manihot*, being thoroughly purified from its poisonous juice.—*Cassava* is the same substance modified while hot by heat.—*Sago* is made from the soft central portion of the stem of palm; and *Salep* from the fleshy root of the *Orchis mascula*.

STARCH FROM ICELAND MOSS.—The lichen called *Cetraria Islandica*, purified by a little cold solution of potash from a bitter principle, yields, when dried in water, a slimy and nearly colorless liquid, which gelatinizes on boiling, and dries up to a yellowish amorphous mass, which does not dissolve in cold water, but merely softens and swells. A solution of this substance in warm water is not affected by iodine, although the jelly is turned blue. It is precipitated by alcohol, lead acetate, and infusion of galls, and converted into glucose by boiling with dilute sulphuric acid. According to Mulder, it contains $C_6H_{10}O_5$. The jelly from certain algae, as that of gelon, and the so-called *Carrageen moss*, closely resembles the above.

Inulin.—This substance which differs from common starch in some important particulars, is found in the root of *Inula Helenum*, *Helianthus tuberosus*, *Dahlia*, and several other plants: it may be easily obtained by washing the rasped root on a sieve, and allowing the inulin to settle down from a liquid; or by cutting the root into thin slices, boiling these in water, and filtering while hot; the inulin separates as the solution cools. It is a white, amorphous, tasteless substance, nearly insoluble in cold water, but only dissolved by the aid of heat; the solution is precipitated by alcohol, but not by acetate of lead or infusion of galls. Iodine colors it brown, which has the same percentage composition as common starch. By boiling with dilute acids, it is completely converted into levulose (p. 622).

Glycogen, $nC_6H_{10}O_5$, was obtained by Bernard from the liver of several animals (calf or pig) by exhaustion with water and precipitating with boiling alcohol. The precipitate is purified by boiling with dilute

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Secondly, the present study is limited in that it only considers the effects of the independent variable on the dependent variable. It would be more useful if the study had also considered the effects of the independent variable on the other variables in the model. This would have allowed the researcher to determine the relative importance of the independent variable in explaining the variance in the dependent variable.

[illegible]

There is another method of preparing this substance from starch which demands particular notice. Following this, the only one in the art of preparation, is based on certain small portions of a particular vegetable substance, and is prepared, formed on this particular period from the point of vegetable substance. This substance is the substance due to the action of starch and at a temperature much less than that of the starch. When a large volume of starch is prepared, there is a great deal of starch present of such polymers, and the starch is kept in the starch. It is completely infusible in water, and in the space of a few minutes from the point of starch and starch. If a greater degree of heat is employed, the substance is completely infusible in water and starch. Very little is known respecting these points of starch, and it is a matter of doubt.

The cleavage of starch or dextrin into sugar, whether produced by the action of dilute acids or by diastase, takes place quite independently of the oxygen of the air, and is uncompensated by any secondary process. The acid takes no direct part in the reaction; it may, if not volatilized, be withdrawn without loss after the experiment. The whole reaction has to do with the starch and the elements of water, a fixation of the latter entering in the new product, as will be seen on comparing the composition of

starch and glucose. Dextrin itself has exactly the same composition as the original starch.

It was formerly supposed that, in the action of acids [or of diastase] upon starch, the starch is first converted into dextrin by a mere alteration of physical structure, and that the dextrin then takes up the elements of water, and is converted into glucose, this second stage of the process occupying a much longer time than the first; but from the experiments of Musculus* it appears that when the conversion is effected by a dilute acid, both dextrin and glucose are produced at the very commencement of the reaction, and always in the proportion of 1 molecule of glucose to 2 molecules of dextrin: whence it may be inferred that the molecule of starch contains $C_{36}H_{60}O_{15}$, and that it is resolved into glucose and dextrin by taking up a molecule of water:



and that the dextrin, after several hours' boiling, is completely converted into glucose, which is therefore the sole ultimate product of the reaction. When malt extract is used as the converting agent the starch is first resolved into dextrin and maltose (p. 629), in various proportions according to the temperature and other conditions of the reaction; and the dextrin afterwards very gradually converted into maltose.†

Dextrin is used in the arts as a substitute for gum; it is sometimes made in the manner above described, but more frequently by heating dry potato-starch to $400^{\circ}C.$ ($752^{\circ}F.$), by which it acquires a yellowish tint and becomes soluble in cold water. It is sold in this state under the name of *British Gum*.

Cellulose, $nC_6H_{10}O_5$, probably $C_{18}H_{30}O_{15}$; also called *Lignin*.—This substance constitutes the fundamental material of the structure of plants: it is employed in the organization of cells and vessels of all kinds, and forms a large proportion of the solid parts of every vegetable. It must not be confounded with *lignum* or *woody tissue*, which is in reality cellulose with other substances superadded, encrusting the walls of the original membranous cells, and conferring stiffness and inflexibility. Pure cellulose, on the other hand, has the same percentage composition as starch; but woody tissue, even when freed as much as possible from coloring matter and resin by repeated boiling with water and alcohol, yields, on analysis, a result indicating an excess of hydrogen above that required to form water with the oxygen, besides traces of nitrogen.

The properties of cellulose may be conveniently studied in fine linen and cotton, which are almost entirely composed of it, the associated vegetable principles having been removed or destroyed by the variety of treatment to which the fibre has been subjected. Pure cellulose is tasteless, insoluble in water and alcohol, and absolutely innutritious: it is not sensibly affected by boiling water, unless it happens to have been derived from a soft or imperfectly developed portion of the plant, in which case it is disintegrated and rendered pulpy. Dilute acids and alkalies exert but little action on the cellulose, even at a boiling temperature; strong oil of vitriol converts it, in the cold, into a nearly colorless, adhesive substance, which dissolves in water, and presents the characters of dextrin. This transformation may be conveniently effected by very slowly adding concentrated sulphuric acid to half its weight of lint, or linen cut into small shreds, taking care to avoid any rise of temperature, which would be

* Comptes Rendus, l. 785; Rev. 191; Ann. Ch. Phys. [3], ix. 208; [4], v. 177.

† O'Sullivan, Chem. Soc. J. 1870, ii. 125.

attended with charring or blackening. The mixing is completed by trituration in a mortar, and the whole left to stand a few hours; after which it is rubbed up with water, warmed, and filtered from a little insoluble matter. The solution may then be neutralized with chalk, and agitated. The gummy liquid retains lime, partly in the state of sulphate, and partly in combination with sulpholignic acid, an acid composed of the elements of sulphuric acid in union with those of cellulose. If the liquid, previous to the neutralization, be boiled during three or four hours, and the water replaced as it evaporates, the dextrin becomes entirely changed into glucose. Linen rags may, by these means, be made to furnish more than their own weight of that substance.

If a piece of unsized paper be dipped for a few seconds into a mixture of 2 volumes of concentrated sulphuric acid and 1 volume of water, and then thoroughly washed with water and dilute ammonia, a substance is obtained which resembles parchment, and has the same composition as cellulose; it occurs in commerce under the name of parchment paper (papyrin). An excellent application of this substance in diffusion experiments is mentioned on p. 144.

Cellulose dissolves in an ammoniacal solution of cupric oxide (prepared by dissolving basic cupric carbonate in strong ammonia), from which it is precipitated by acids in colorless flakes.

Cellulose is not colored by iodine.

Xyloidin and Pyroxylin.—When the starch is mixed with nitric acid of specific gravity 1.5, it is converted, without disengagement of gas, into a transparent, colorless jelly, which, when put into water, yields a white curdy, insoluble substance: this is *xyloidin*. When dry, it is white and tasteless, insoluble even in boiling water, but freely dissolved by dilute nitric acid, and the solution yields oxalic acid when boiled. Other substances belonging to the same class also yield xyloidin; paper dipped into the strongest nitric acid, quickly plunged into water, and afterwards dried, becomes in great part so changed: it assumes the appearance of parchment, and becomes highly combustible.

If pure finely divided cellulose, such as cotton-wool, be steeped for a few minutes into a mixture of nitric acid of sp. gr. 1.5 and concentrated sulphuric acid, then squeezed, thoroughly washed, and dried by very gentle heat, it will be found to have increased in weight about 70 per cent., and to have become highly explosive, taking fire at a temperature not much above 149° C. (300° F.), and burning without smoke or residue. This is *pyroxylin*, the *gun-cotton* of Schönbein.

Xyloidin and pyroxylin are substitution-products consisting of starch and cellulose in which the hydrogen is more or less replaced by nitril, NO_2 . Xyloidin consists of $\text{C}_6\text{H}_5(\text{NO}_2)_3\text{O}_5$, or $\text{C}_{12}\text{H}_7(\text{NO}_2)_6\text{O}_{15}$. Of pyroxylin several varieties are known, distinguished by their different degrees of stability and solubility in alcohol, ether, and other liquids. According to Hadow,* the three principal varieties are:—

α .— $\text{C}_{12}\text{H}_{11}(\text{NO}_2)_3\text{O}_{15}$, or $\text{C}_6\text{H}_5(\text{NO}_2)_3\text{O}_5$, insoluble in a mixture of ether and alcohol, but soluble in ethylic acetate. It is produced by repeated immersion of cotton-wool in a mixture of 2 molecules of nitric acid, HNO_3 , 2 molecules of oil of vitriol, H_2SO_4 , and 3 molecules of water.

β .— $\text{C}_{12}\text{H}_{11}(\text{NO}_2)_4\text{O}_{15}$, soluble in ether-alcohol, insoluble in glacial acetic acid. Produced when the acid mixture contains half a molecule more water than in α .

γ .— $\text{C}_{10}\text{H}_{11}(\text{NO}_2)_7\text{O}_{15}$ (Gladstone's *cotton-xyloidin*), soluble in ether and in

* Chem. Soc. Journal, vii. 201. — A series of elaborate and valuable researches on gun cotton has been published by Abel (Proceed. Royal Soc., xv. 182; Chem. Soc. Journ., [2], xv. 319).

the acid. Produced when the acid mixture contains one molecule of tunicin than in a.

of these, which consist of *trinitrocellulose*, is the most explosive, and the least liable to spontaneous decomposition. It is the adapted for use as an explosive agent, and is especially distinguished as "gun-cotton." From the experiments of General von Lenk, of service, it appears that, to insure the uniform production of this compound, the following precautions are necessary:— 1. Steeping and perfect desiccation of the cotton previously to its use in the mixed acids. 2. The employment of the strongest acids in commerce. 3. The steeping of the cotton in a fresh strong acid after the first immersion and partial conversion into gun-cotton. The continuance of the steeping for forty-eight hours. 5. The purification of the gun-cotton thus produced from every trace of acid by washing the product in a stream of water for several weeks; or by a weak solution of potash may be used, but this is not

tion of the less highly nitrated compounds in alcohol and ether solution. This solution, when left to evaporate, dries up to a thin, transparent, adhesive membrane: it is employed with advantage in surgery as an air-tight covering for wounds and burns. It is largely used in photography (p. 96).

$C_6H_{10}O_6$, is a substance closely resembling vegetable cellulose, and is identical therewith, occurring in the mantle of *Ascidians* (*Salpaxia*, etc.), from which it may be separated by boiling the material with hydrochloric and then with strong potash-solution, and washing with water. When treated with strong sulphuric acid, it deliquesces to a colorless liquid, which, after boiling with water, is found to be glucose.

Gum-arabic, which is the produce of several species of acacia in Egypt and Arabia, may be taken as the type of this class of resins. When pure, it forms white or slightly yellowish irregular masses, destitute of crystalline structure, and break with a smooth conchoidal fracture. It is soluble in cold water, forming a viscid, adhesive solution. It consists of the potassium and calcium salts of arabic acid, which may be precipitated from the aqueous solution of hydrochloric acid and alcohol, as a white amorphous powder, when dried at $100^\circ C.$, has the composition $C_6H_{10}O_6 + \frac{1}{2}H_2O$, and is therefore isomeric with cane-sugar; at $150^\circ C.$ it gives off all its water, leaving a residue having the composition $C_6H_8O_5$.

Arabin contains 70.4 per cent. arabin and 17.6 water, the remaining consisting of metallic salts, silica, iron oxide, etc. Its aqueous solution gives the plane of polarization to the left, and gives precipitates with lead acetate, copper salts, etc. Arabin is oxidized by nitric acid and saccharic acids. Heated with dilute sulphuric acid, it is converted into a non-fermentable glucose called *arabinose*, which crystallizes in rhombic needles, and exhibits strong dextro-rotation.

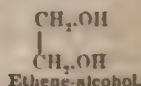
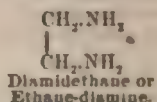
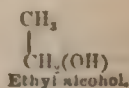
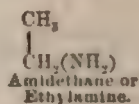
Gum, obtained from a species of acacia growing in Senegal, is very similar to gum-arabic, but usually occurs in larger lumps. It contains about 70 per cent. arabin, 1.6 water, and 2 or 3 per cent. of saline matters. It is somewhat stronger mucilage than gum-arabic, and is much used in painting for thickening colors and mordants.

Salp, abundant in linseed, in the roots of the mallow, in *salp*, the root of *Orchis mascula*, and in other plants, differs in some respects

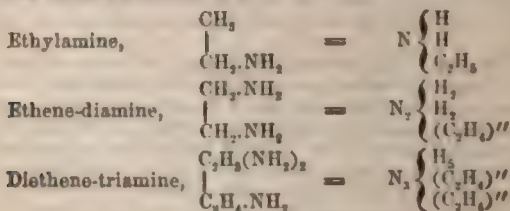
from gum-arabic, although it agrees in the property of dissolving in cold water. The solution is less transparent than that of gum, and is precipitated by neutral lead acetate. *Gum-tragacanth*, from *Astragalus creus*, a tree growing in Armenia and the north of Persia, is chiefly composed of a kind of mucilage called *bassoria*; it does not dissolve in water, but merely softens and assumes a gelatinous aspect. It is dissolved by caustic alkali. *Goma* is the insoluble portion of the gum of the cherry tree; it resembles bassoria. The composition of these various substances agrees closely with that of starch. Mucilage treated with acids yields dextrose.

AMINES.

These are compounds which may be derived from hydrocarbons by substitution of the univalent radicle amidogen, NH_2 , for an equivalent quantity of hydrogen, or from the alcohols by similar substitution of NH_2 for OH : they are called monamines, diamines, triamines, etc., according to the number of amidogen groups thus introduced; thus from ethane and the corresponding alcohols are derived the following monamine and diamine:



The amines are basic compounds, capable of uniting with acids and forming salts which bear a close resemblance to the salts of ammonia; the amines themselves in the free state are also very much like ammonia, being volatile bodies having a more or less ammoniacal odor and alkaline reaction. They may, in fact, be regarded as derivatives of ammonia, formed by substitution of alcohol radicles, univalent or multivalent, for an equivalent quantity of hydrogen, in a single, double, or triple molecule of ammonia, NH_3 , N_2H_6 , N_3H_9 , etc., e. g.:



MONAMINES.

These bases are derived from a single molecule of ammonia, NH_3 . Now this molecule may give up one, two, or all three of its hydrogen-atoms in exchange for univalent alcohol-radicles,—methyl and its homologous, for

le,—producing primary, secondary, and tertiary amines. B, C denote three such alcohol-radicles, the amines formed by substituting them for hydrogen in ammonia will be represented by the general formulae:



Primary.



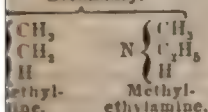
Secondary.



Tertiary.

In secondary and tertiary amines the alcohol-radicles denoted by A, may be either the same or different; for example:

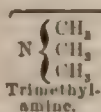
Secondary.



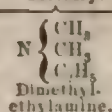
Ethylamine.

Methyl-ethylamine.

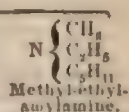
Tertiary.



Trimethylamine.

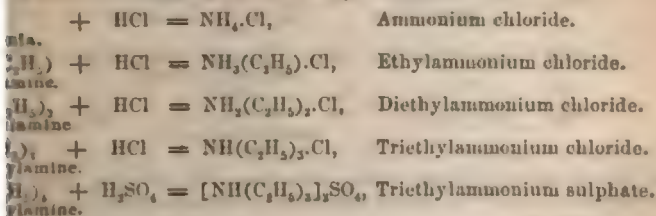


Dimethyl-ethylamine.



Methyl-ethyl-awylamine.

Salts of these amines are analogous in composition to the ammonium-salts, and, like the latter, may be regarded either as compounds of ammonium-bases with acids, or of ammonium-molecules with halogen elements and radicles analogous thereto (see p. 480); thus:



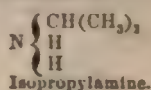
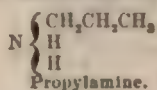
These salts when heated with potash, give off the amine, just as ammonium-salts give off ammonia.

Tertiary amines can unite with the chlorides, etc., of alcohol-radicles in the same manner as with acids: thus triethylamine, $\text{N}(\text{C}_2\text{H}_5)_3$, unites with ethyl iodide, $\text{C}_2\text{H}_5\text{I}$, forming a compound which may be regarded either as *triethylamine ethiodide*, $\text{N}(\text{C}_2\text{H}_5)_3 \cdot \text{C}_2\text{H}_5\text{I}$, or as *tetraethylammonium iodide*, $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$. Now this iodide, when heated with potash, does not give off ammonia or a volatile ammonia-base; but when heated with oxide and water, it is converted, by exchange of iodine for hydroxyl, into a strongly alkaline base, called *tetraethylammonium hydroxide*, which may be obtained in the solid state, and exhibits reactions closely analogous to those of the fixed caustic alkalis. Its formation is represented by the equation:

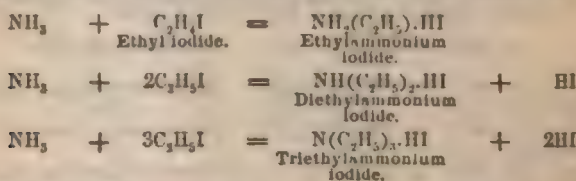


Further, this base can exchange its hydroxyl for chlorine, bromine, and acid radicles, just like potash or soda, forming solid crystallizable salts like the iodide above mentioned. These compounds, containing four equivalents of alcohol-radicle, are, in fact, analogous in every respect to ammonium-salts, excepting that the corresponding hydroxides are capable of existing in the solid state, whereas ammonium hydroxide, $\text{NH}_4(\text{OH})$, as soon as formed, enters into ammonia and water. The radicles C_2H_5 , etc., corresponding with ammonium, are not known in the free

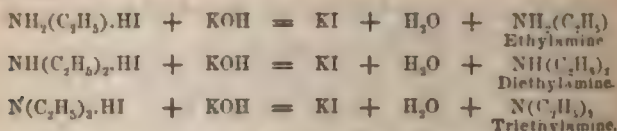
The monamines containing more than one carbon-atom are susceptible of isomeric modifications similar to those of the alcohols, and depending on the number of alcohol-radicles in the molecule: thus ethylamine, $\text{CH}_3(\text{C}_2\text{H}_5)_1$, is isomeric with dimethylamine, $\text{NH}(\text{CH}_3)_2$; propylamine, $\text{NH}_2(\text{C}_3\text{H}_7)_1$, is isomeric with methyl-ethylamine, $\text{NH}(\text{CH}_3)(\text{C}_2\text{H}_5)_1$, and with trimethylamine, $\text{N}(\text{CH}_3)_3$, etc., etc., the number of possible modifications of course increasing with the complexity of the molecules. Moreover, a monamine, either primary, secondary, or tertiary, may admit of modification in the alcohol-radicle itself; thus the primary monamide, $\text{NH}_2(\text{C}_3\text{H}_7)_1$, may exhibit the two following modifications:—



General Modes of Formation.—1. By heating the iodides or bromides of the alcohol-radicles to 100° in sealed tubes with alcoholic ammonia. The hydrogen of the ammonia is then replaced by the alcohol-radicle, forming a mixture of primary, secondary, and tertiary amines, which unite with the halogen-acid, produced at the same time, to form ammonium salts, thus:—

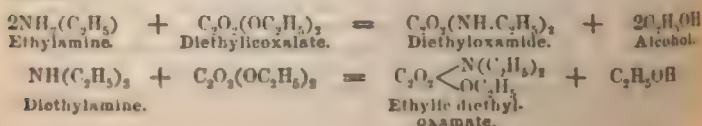


From the mixture of ammonium salts thus obtained, the three amines, being volatile, may be at once separated by distillation with aqueous potash or soda:—

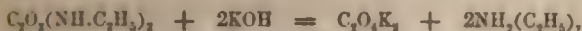


while the tetrethylammonium iodide remains unaltered, but may be converted into the corresponding hydroxide, $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$, by the action of moist silver oxide in the manner already explained.

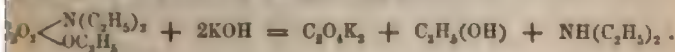
The primary, secondary, and tertiary amines cannot be separated by fractional distillation, but their separation may be effected by the following process, devised by Dr. Hofmann. The mixture is treated with diethyl oxalate (oxalic ether), whereby the primary amine is converted into diethyloxamide (see *Amines*), which is easily soluble in water, while the diethylamine is converted into the ethylic ether of diethyloxamic acid, which is insoluble in water, and the triethylamine remains unaltered:—



distilling the product of this reaction, the unaltered triethylamine passes over. From the residue, water extracts the diethyloxamide, which is resolved by boiling with potash into oxalic acid and diethylamine:—

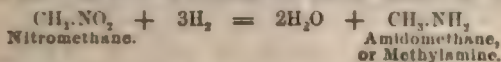


the diethyloxamic ether, which is not dissolved by the water, yields, on distillation with potash, diethylamine:—

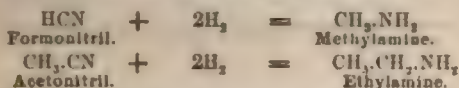


The primary amines may also be obtained by the following processes:—

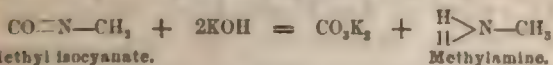
By the action of nascent hydrogen on the nitroparaffins:—



By the action of nascent hydrogen on the nitrils (azoparaffins, p. 6—)



By distilling an isocyanic or isocyanuric ether with potash-lye:—



This reaction, which is exactly analogous to the formation of ammonia from cyanic acid, ($\text{CO}=\text{NH} + 2\text{KOH} = \text{CO}_2\text{K}_2 + \text{NH}_3$), is that by which the primary amines were first obtained by Wurtz.

Amines are also produced by special reactions, as by the decomposition of the more complex nitrogen-compounds and of amido-acids.

Properties and Reactions.—The amines, as already observed, bear a strong resemblance to ammonia. The lower members of the group are gases, very soluble in water, and having a strong ammoniacal odor; they are distinguished from ammonia by their ready combustibility. The higher members are liquids, more or less oily. Amines expel ammonia from its salts when heated with them, and in like manner the monamines are released by the diamines, and these by the triamines: hence it might be inferred that the basic power of an amine increases with the number of radical-entities which it contains; but in this, as in many similar cases, the expulsion of one base or acid by another is a question of relative volatility as well as of strength of combination.

Amines form double salts with *platinic chloride*, *auric chloride*, and other metallic haloid salts, exactly similar to those of ammonia, e. g.:

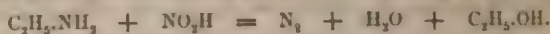


They can also replace ammonia in the alums, and in the salts of platinum, cuprammonium, etc. Examples of such compounds are:



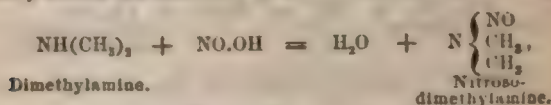
Platosodiethyldiammonium chloride. $\text{Pt} \begin{matrix} \text{NH}_2\text{NH}_2(\text{C}_2\text{H}_5)\text{Cl} \\ \text{NH}_2\text{NH}_2(\text{C}_2\text{H}_5)\text{Cl} \end{matrix}$

Primary amines treated with *nitrous acid* (or their haloid salts with potassium nitrite) are converted into the corresponding alcohols, thus



This reaction—analogue to the resolution of ammonium nitrite into ammonia and water ($\text{NH}_3 + \text{NO}_2\text{H} = \text{N}_2 + 2\text{H}_2\text{O}$)—affords, as already served (p. 579), the means of passing from one alcohol of a series to the next highest: thus methyl alcohol yields methyl cyanide or formonit $\text{C}_2\text{H}_5\text{N}$; this may be converted by nascent hydrogen into ethylamine $\text{C}_2\text{H}_5\text{NH}_2$; and this base, as above, into ethyl alcohol.

Secondary amines are converted by nitrous acid into nitroso-compounds



and tertiary amines are but slightly attacked by nitrous acid.

METHYL BASES.

Methylamine or **Amidomethane**, $\text{CH}_3\text{N} = \text{H}_2\text{C} - \text{NH}_2$. $\text{N} \begin{matrix} \text{H}_2 \\ \text{CH}_3 \end{matrix}$. This base may be formed by either of the general reactions above given, also by the decomposition of certain natural alkaloids, morphine, narcotine, and theine; but it is best prepared by heating methyl isocyanate with potash in a retort attached to a receiver cooled by freezing mixture. The distillate, which is an aqueous solution of methylamine, is saturated with hydrochloric acid, and evaporated to dryness, whereby a crystalline residue is obtained consisting of methylammonium chloride; and this when distilled with dry lime yields methylamine in form of a gas, which must be collected over mercury.

Methylamine is a colorless gas, having an ammoniacal and slightly fishy odor, a specific gravity of 1.08, and condensing to a liquid at -16° (0.40°F.). It is the most soluble of all gases, one volume of water at 15°C. (59.6°F.) absorbing 1040 volumes of the gas: it is likewise very readily absorbed by charcoal. It is distinguished from ammonia by its odor, by the facility with which it burns. In its deportment with acids and other substances, however, it bears the closest resemblance to ammonia. Its aqueous solution also possesses all the properties of aqueous ammonia, excepting that it does not dissolve the oxides of nickel, cobalt, or cadmium. Iodine added to the aqueous solution, throws down a dark-red precipitate of di-iodomethylamine, while methylammonium iodide remains in solution.



Bromine acts in a similar manner. The gas passed over heated potassium is resolved into cyanogen and hydrogen:



The salts of methylamine are easily soluble in water. The hydrochloride $\text{CH}_3\text{N.HCl}$, crystallizes in large deliquescent laminae, which melt at 11°C. , and distil without decomposition. With platinum chloride it forms

crystalline precipitate of the *platinochloride*, $2(\text{CH}_3\text{N.HCl}).\text{PtCl}_4$, and with auric chloride the double salt, $\text{CH}_3\text{N.HCl.AuCl}_3$, which crystallizes in scales. Methylamine also forms platinum-bases analogous to the *iso*-platinum compounds (p. 442).

Methylamine, $\text{C}_2\text{H}_7\text{N} = \text{NH}(\text{CH}_3)_2$, isomeric with ethylamine, is obtained by heating ammonia with methyl iodide, and separated from similarly formed methylamine and trimethylamine by means of oxalic acid (p. 638). It is a gas which dissolves easily in water, and condenses at below $+8^\circ \text{C}$. (46.4°F .). Its *platinochloride* crystallizes in needles.

Dimethylamine, $\text{C}_3\text{H}_9\text{N} = \text{N}(\text{CH}_3)_2$, isomeric with propylamine and ethylamine, is obtained in perfect purity by the action of heat on diethyl-ammonium hydroxide, which is thereby completely resolved into methylamine and methyl alcohol:



It is produced by distilling codeine and narcotine with potash, and is found in large quantity in herring-pickle, the peculiar odor of which is due to its presence. It is a liquid easily soluble in water, and boiling at 36°C . (96.8°F .). Its salts are soluble; the hydrochloride very deliquescent.

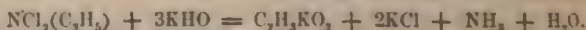
Trimethyl-ammonium compounds.—The *iodide*, $\text{N}(\text{CH}_3)_3\text{I}$, may be prepared by adding methyl iodide to trimethylamine. The two substances unite with a sort of explosion. It is more easily prepared, however, by digesting methyl iodide with an alcoholic solution of ammonia. In this reaction a mixture of the iodides of ammonium, methyl-ammonium, dimethyl-ammonium, trimethyl-ammonium, and tetramethyl-ammonium is produced. The first and last compounds are formed in largest quantity, and may be separated by crystallization, the iodide of tetramethyl-ammonium being but sparingly soluble in water. It crystallizes in hard, flat plates of dazzling whiteness. The *hydroxide*, $\text{N}(\text{CH}_3)_3\text{OH}$, resembles the corresponding ethyl-compound (*infra*), and is decomposed by heat, as above, into methyl alcohol and trimethylamine.

ETHYL BASES.

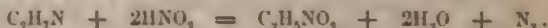
Ethylamine or Amido-ethane, $\text{C}_2\text{H}_5\text{N} = \text{H}_2\text{C}-\text{CH}_2(\text{NH}_2) = \text{N} \begin{Bmatrix} \text{H}_2 \\ \text{C}_2\text{H}_5 \end{Bmatrix}$, is obtained either by heating ethyl isocyanate with potash, or by digesting ethyl cyanide or iodide with alcoholic ammonia, and treating the mixture with ether, thereby produced with oxalic ether in the manner already described. It is a very mobile liquid, having a specific gravity of 0.6964 at 80°C . (176°F .), boiling at 19°C . (66.2°F .), and giving off an inflammable vapor of specific gravity 1.37. It has a most powerful ammoniacal odor, and restores the blue color to reddened litmus-paper. It produces white clouds with hydrochloric acid, is absorbed by water with great facility, and reacts like ammonia with metallic salts, precipitating the oxides of magnesium, aluminium, iron, manganese, bismuth, chromium, tin, lead, and mercury; and forming with zinc-salts a white precipitate, which is soluble in excess. It dissolves silver chloride, and with copper-salts a blue precipitate, which is soluble in excess of ammonia.

By adding ethylamine to *oxalic ether*, a white precipitate of diethylox-
 $\text{C}_2\text{O}_2(\text{NH.C}_2\text{H}_5)_2$, is produced. Treated with *chlorine*, it yields

ethylammonium chloride and dichlorethylamine, $\text{NCl}_2\text{C}_2\text{H}_5$, a yellow liquid which has a penetrating, tear-exciting odor, and when treated with potash is converted into ammonia, potassium acetate, and potassium chloride:



Ethylamine is decomposed by *nitrous acid*, with formation of ethyl nitrite and evolution of nitrogen:



On passing the vapor of *cyanic acid* into a solution of ethylamine, the liquid becomes hot, and deposits, after evaporation, crystals of ethyl-urea: $\text{C}_2\text{H}_7\text{N} + (\text{NHO} = \text{C}_2\text{H}_5\text{N}_2\text{O} \text{ or } \text{C}_2\text{H}_5(\text{C}_2\text{H}_5)\text{N}_2\text{O})$.

The salts of ethylamine resemble those of ammonia and of methylamine. The *hydrochloride*, $\text{NH}_2(\text{C}_2\text{H}_5)\cdot\text{HCl}$, crystallizes in large deliquescent plates, melting at 80°C . (176°F .); the *platinochloride*, $2\text{NH}_2(\text{C}_2\text{H}_5)\text{Cl}\cdot\text{PtCl}_4$, in orange-yellow scales.

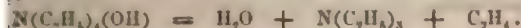
Diethylamine, $\text{C}_4\text{H}_{11}\text{N} = \text{NH}(\text{C}_2\text{H}_5)_2$.—A mixture of the solutions of ethylamine and ethyl bromide, heated in a sealed tube for several hours, solidifies to a crystalline mass of diethylammonium bromide: $\text{NH}_2(\text{C}_2\text{H}_5) + \text{C}_2\text{H}_5\text{Br} = \text{NH}_2(\text{C}_2\text{H}_5)_2\text{Br}$. This bromide, distilled with potash, yields diethylamine as a colorless liquid, still very alkaline, and soluble in water, but less so than ethylamine. This compound boils at 57°C . (134.6°F .). It forms beautifully crystallizable salts with acids. A solution of diethylammonium chloride forms with platinum chloride a very soluble double salt, $2\text{NH}_2(\text{C}_2\text{H}_5)_2\text{Cl}\cdot\text{PtCl}_4$, crystallizing in orange-red grains, very different from the orange-yellow leaves of the corresponding ethyl-ammonium salt.

Diethylamine behaves with cyanic acid like ammonia and ethylamine, giving rise to diethyl-urea, $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{N}_2\text{O}$.

Triethylamine, $\text{C}_6\text{H}_{13}\text{N} = \text{N}(\text{C}_2\text{H}_5)_3$.—The formation of this body is perfectly analogous to that of ethylamine and of diethylamine. On heating for a short time a mixture of diethylamine with ethyl bromide in a sealed glass tube, a beautiful fibrous mass of triethylammonium bromide is obtained, from which the triethylamine may be separated by potash. Triethylamine is a colorless, powerfully alkaline liquid, boiling at 89°C . (192.2°F .). Its salts crystallize remarkably well. With platinum chloride it forms a very soluble double salt, $2\text{NH}(\text{C}_2\text{H}_5)_3\text{Cl}\cdot\text{PtCl}_4$, which crystallizes in magnificent, large, orange-red rhombs.

Tetretethylammonium compounds.—When anhydrous triethylamine is mixed with dry ethyl iodide, a powerful reaction ensues, the mixture boils, and solidifies on cooling to a white crystalline mass of tetretethylammonium iodide: $\text{N}(\text{C}_2\text{H}_5)_3 + \text{C}_2\text{H}_5\text{I} = \text{N}(\text{C}_2\text{H}_5)_4\text{I}$. This iodide is readily soluble in hot water, from which it separates on cooling in beautiful crystals of considerable size. It is not decomposed by potash, but may be boiled with the alkali for hours without yielding a trace of volatile base. The iodine may, however, be readily removed by treating the solution with silver-salts. If in this case silver sulphate or nitrate be used, we obtain, together with silver iodide, the sulphate or nitrate of tetretethylammonium, which crystallizes on evaporation: on the other hand, if the iodide be treated with freshly precipitated silver oxide, the hydroxide of tetretethylammonium, $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$, is separated. On filtering off the silver precipitate, a clear colorless liquid is obtained, which contains the isolated base in solution. It has a strongly alkaline reaction, and in

ter taste. The solution of tetrethyl-ammonium hydroxide has the analogy to potash and soda. Like these substances, it de-epidermis and saponifies fatty substances, with formation of true lith metallic salts it exhibits exactly the same reactions as potash. Giving a solution of the base in a vacuum, long slender needles are obtained, consisting of the hydroxide with a certain amount of crystalline water. After some time these needles disappear, and a semi-solid is left, which is the anhydrous base. A concentrated solution of the compound in water may be boiled without decomposition, but on the dry substance, it is decomposed into triethylamine, water, and hydrogen:



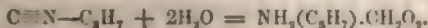
or salts of tetrethylammonium are obtained by treating the hydrocyanic acids: several of them form beautiful crystals. The *platinocyanide*, $N(C_2H_5)_4[Cl]_2.PtCl_4$, crystallizes in orange-yellow octohedrons, soluble in water, less soluble in alcohol and ether.

Members of the series $C_nH_{2n+3}N$, which contain more than three carbon, admit, as already observed, of isomeric modifications, and the structure of their alcohol-radicles.

Propylamine (normal), $C_3H_7N = N \begin{Bmatrix} CH_2CH_2CH_3 \\ H \end{Bmatrix}$, produced by hydrogenation of propionitril (ethyl cyanide), C_2H_5N , or by the action of sodium on the mixture of propyl isocyanate and isocyanurate obtained by distilling normal propyl iodide with silver cyanate, is a strongly caustic liquid, boiling at $50^\circ C.$ ($122^\circ F.$), and having a specific gravity of 0.70. The *platinocyanide*, $2(C_3H_7N.HCl).PtCl_4$, crystallizes in low monoclinic prisms.

The *nitrate*, $C_3H_7N.NO_3$, is resolved by heat into pseudopropyl alcohol, and water, $CH_3-CH_2-CH_2(NH_2) + NO_2H = CH_3-CHOH-CH_2I_2O$.

Isopropylamine, $CH_3-CH.NH_2-CH_3$, or $N \begin{Bmatrix} CH(CH_3)_2 \\ H \end{Bmatrix}$, is produced also by the action of hydrochloric acid on isopropyl isocyanide:—



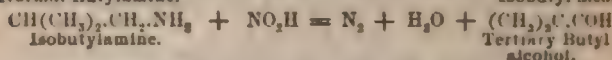
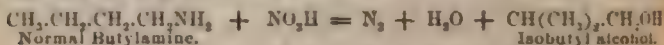
It is liberated from this salt by successive treatment with hydrochloric acid and potash, is a sweetish ammoniacal liquid, boiling at $32^\circ C.$ Its *platinocyanide* crystallizes in golden-yellow scales or flat-plates.

Butylamines.—Of primary butylamine, $C_4H_{11}N$, there are three isomers, viz.:—

Normal Butylamine, $CH_3.(CH_2)_3.NH_2$, obtained by the action of hydrogen on normal propyl cyanide or butyro-nitril, $CH_3(CH_2)_3C \equiv N$, is a colorless, hygroscopic, fuming liquid, boiling at $75.5^\circ C.$ and having a specific gravity of 0.755 at $0^\circ C.$ Nitrous acid converts it into isobutyl alcohol, $CH(CH_3)_2-CH_2OH$.

Isobutylamine, $CH(CH_3)_2.CH_2.NH_2$, is obtained by distilling a mixture of potassium isobutylsulphate with potassium cyanate, and treating the product with isobutyl isocyanate with potash. It boils at $68^\circ C.$ ($154.4^\circ F.$)

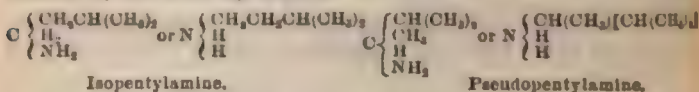
F.), and has a specific gravity of 0.7357 at 15° C. (59° F.). With nitrous acid it yields tertiary butyl alcohol or trimethyl carbinol, $(\text{CH}_3)_3\text{COH}$. Now it has been already stated that normal butylamine similarly treated is converted into isobutyl alcohol, and normal propylamine into isopropyl alcohol. Hence it appears that the action of nitrous acid on primary amines gives rise to the alcohol of a radicle containing one or more methyl-group than the original amines:—



3. Tertiary Butylamine, or Katabutylamine, $(\text{CH}_3)_3\text{C.NH}_2$, is prepared by heating isobutyl iodide with dry silver cyanate, mixing the resulting solid compound of silver iodide and isobutyl cyanate with finely pulverized potassium hydroxide, and distilling the mixture by small quantities at a time. It is a liquid boiling at 45–46° C. (113–114.8° F.), and having a specific gravity of 0.6987 at 15° C. (59° F.).

Diethylamine, $\text{NH}(\text{C}_2\text{H}_5)_2$, and Triethylamine, $\text{N}(\text{C}_2\text{H}_5)_3$, are obtained as bye-products in the preparation of normal valeric acid by the action of alcoholic potash on normal butyl cyanide. The former boils at 160° C. (320° F.), the latter between 211° C. (411.8° F.) and 215° C. (419° F.).

Pentylamines.—Of primary pentylamines, $\text{C}_5\text{H}_{13}\text{N}$, there are two known modifications, viz., isopentylamine or amylamine, derived from the ordinary amyl alcohol of fermentation, and pseudopentylamine, derived from isopropyl-methyl carbinol (p. 586). They are represented by the following formula:—

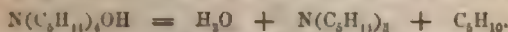


Isopentylamine or Ordinary Amylamine, is obtained by distilling isopentyl isocyanate or isocyanurate, or primary isopentyl-carbamide, $\text{CON}_2\text{H}_4(\text{C}_5\text{H}_{11})$, with potash; pseudo-pentylamine in like manner from secondary isopentyl-carbamide, $\text{CON}_2\text{H}_2(\text{CH}_3)(\text{C}_5\text{H}_9)$. Both are colorless liquids, of penetrating ammoniacal odor, and slightly soluble in water, to which they impart an alkaline reaction. Amylamine boils at 95° C. (203° F.), and has a specific gravity of 0.7503 at 18° C. (64.4° F.); pseudopentylamine boils at 78.5° C. (173.3° F.), and has a specific gravity of 0.745 at 0° C. Platinochloride of amylamine crystallizes in golden-yellow scales, that of pseudopentylamine in fine crystals derived from a monoclinic prism. The aurochloride of pseudopentyl, $\text{C}_5\text{H}_{14}\text{N.AuCl}_2$, forms large yellow monoclinic crystals.

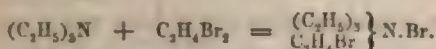
Diamylamine, $\text{C}_{10}\text{H}_{23}\text{N} = \text{NH}(\text{C}_5\text{H}_{11})_2$.—An aromatic liquid, less soluble in water, and less alkaline than amylamine. It boils at about 170° C. (336° F.).

Triamylamine, $\text{C}_{15}\text{H}_{33}\text{N} = \text{N}(\text{C}_5\text{H}_{11})_3$.—A colorless liquid, having properties similar to those of the two preceding bases, but boiling at 257° C. (494° F.). The salts of triamylamine are very sparingly soluble in water, and melt, when heated, to colorless liquids, floating upon water.

Trimethylammonium Hydroxide, $C_3H_7NO = N(C_2H_5)_3OH$.—This base is far less soluble than the corresponding bases of the methyl series, and separates as an oily layer on adding potash to the aqueous solution. On evaporating the solution in an atmosphere free from carbonic acid, the alkali may be obtained in splendid crystals of considerable size. When submitted to distillation it splits into water, triethylamine, and amylene:

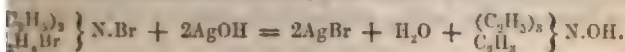


Bromomethyl- and Ethenyl- or Vinyl-bases.—Tertiary amines unite directly with ethene bromide, giving rise to brominated ammonium-bases: *e. g.*,

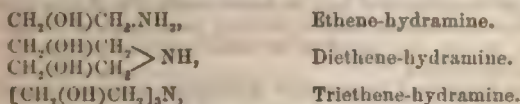


In these compounds, the bromine directly attached to the nitrogen is easily removable by double decomposition, by the action of silver nitrate, for example, whereby the bromide is converted into the nitrate $(C_2H_5)_3\left. \begin{matrix} \\ C_2H_4Br \end{matrix} \right\} N.NO_3$.

In the other bromine-atom is more intimately combined, but this also may be removed by the action of moist silver oxide, the group C_2H_4Br or CH_2Br —being converted, by elimination of HBr , into ethenyl or vinyl $CH_2=CH$, the bromide of triethyl-bromomethyl-ammonium being converted into triethyl-vinyl-ammonium hydroxide:

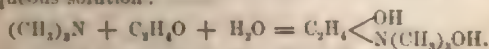


Etheno-bases or Hydramines.—When etheneoxide, $CH_2=O-CH_2$, is treated with aqueous ammonia, 1, 2, or 3 moles of the oxide unite with one mol. ammonia, producing the following



The hydrochlorides of these bases are also formed by the action of ammonia on ethene chlorhydrin, $C_2H_4Cl(OH)$. The bases are separated from one another by fractional crystallization of their hydrochlorides or platinichlorides. They are viscid, alkaline liquids, decomposed by distillation.

Sineoline, $C_3H_{11}NO_2$.—This base, which has the composition of trimethyl-hydrammonium hydroxide, $C_2H_5 \left\langle \begin{matrix} OH \\ N(CH_3)_3 \end{matrix} \right\rangle OH$, is formed synthetically by heating ethene oxide or ethene-chlorhydrin with trimethylamine in aqueous solution:

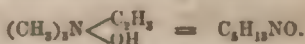


Sineoline exists ready-formed in the animal organism, namely in bile, from which it was first obtained (hence its name); also in the brain, and in the yolk of egg, in both of which it occurs in the form of lecithin, a compound of choline with glycerophosphoric acid and fatty acids. It is also obtained from sinapine, the alkaloid of white mustard, by boiling with caustic soda, and is thence also called sinealine.

Sineoline is a deliquescent substance difficult to crystallize, having a strong

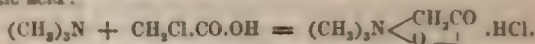
acid reaction, and absorbing carbonic acid from the air. Its *platinochloride*, $2(\text{C}_2\text{H}_5\text{NO}_2.\text{HCl}).\text{PtCl}_4$, crystallizes in fine red-yellow tables, insoluble in alcohol.

Choline heated with hydriodic acid yields the compound $(\text{CH}_3)_3\text{N} \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{I} \end{smallmatrix}$, which, by action of moist silver oxide is converted to trimethyl-vinyl-ammonium hydroxide:



This base, called *neurine*, is very much like choline—from which it differs by H_2O —and likewise exists in the brain.

Betaine, $\text{C}_5\text{H}_{11}\text{NO}_3$, the alkaloid of beet-juice, which has the constitution of trimethyl-glycocine, $(\text{CH}_3)_3\text{N} \begin{smallmatrix} \text{CH}_2.\text{CO} \\ \text{O} \end{smallmatrix}$ (see AMIDES), is also not related to choline, and is formed by oxidation of choline hydrochloride, whence it is also called *oxycholine*, and *oxynurine*. It is formed synthetically, as a hydrochloride, by heating trimethylamine with *acetylchloric acid*:



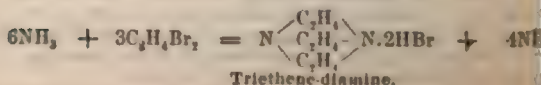
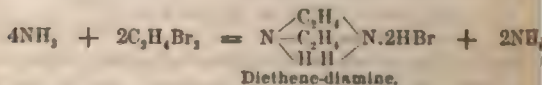
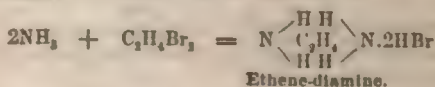
Betaine crystallizes from alcohol in shining deliquescent crystals containing one molecule of water. It has a neutral reaction, a sweetish taste, and is decomposed by boiling alkalis, with evolution of trimethylamine.

DIAMINES.

These are bases derived from a double molecule of ammonia, N_2H_6 , by substitution of bivalent alcohol-radicles for a part or the whole of the hydrogen, or from the paraffins by substitution of two NH_2 -groups for 2 atoms of hydrogen.

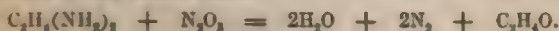
Diamines are formed by the action of ammonia on the chlorides, bromides, and iodides of diatomic alcohol-radicles (olefines).

Ethene-diamines.—By the action of ammonia on ethene diamide, a number of compounds are produced, among which are the hydrobromides of three bases derived from two molecules of ammonia, by substitution of 1, 2, or 3 molecules of ethene, C_2H_4 , for equivalent quantities of hydrogen; thus:



The mixture of hydrobromides thus obtained is decomposed by distillation with potash, and the three diamines which pass over are separated by fractional distillation.

Ethene-diamine, $C_2H_8N_2 = C_2H_4(NH_2)_2 = N_2 \left\{ \begin{smallmatrix} C_2H_4 \\ H_4 \end{smallmatrix} \right\}$, is also produced by the action of tin and hydrochloric acid on dicyanogen: $C_2N_2 + 4H_2 = C_2H_8N_2$. It is a colorless liquid, boiling at $123^\circ C.$ ($253.4^\circ F.$), having a strong alkaline reaction, and ammoniacal odor. Nitrous acid converts it into ethene oxide:



Diethene-diamine, $N_2 \left\{ \begin{smallmatrix} C_2H_4 \\ C_2H_4 \\ H_2 \end{smallmatrix} \right\}$, boils at $170^\circ C.$ ($338^\circ F.$); *triethene-diamine*, $N_2(C_2H_4)_3$, at $220^\circ C.$ ($428^\circ F.$).

These diamines are bi-acid bases, capable of uniting directly with 2 equivalents of an acid. They can also unite with the bromides and iodides of the alcohol-radicles, producing iodides of ammonium bases, thus:

from *Ethene-diamine* are obtained:

| | |
|--|---------------------------------------|
| Iodide of Ethene-diammonium | . $[N_2H_4(C_2H_5)_2]I_2$. |
| Iodide of Diethyl-ethene-diammonium | . $[N_2H_4(C_2H_5)_2(C_2H_5)_2]I_2$. |
| Iodide of Tetraethyl-ethene-diammonium | . $[N_2H_2(C_2H_5)_4(C_2H_5)_4]I_2$. |
| Iodide of Pentethyl-ethene-diammonium | . $[N_2H(C_2H_5)_5(C_2H_5)_5]I_2$. |
| Iodide of Hexethyl-ethene-diammonium | . $[N_2(C_2H_5)_6(C_2H_5)_6]I_2$. |

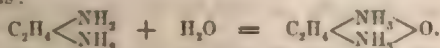
from *Diethene-diamine*:

| | |
|--|---------------------------------------|
| Iodide of Diethene-diammonium | . $[N_2H_4(C_2H_4)_2]I_2$. |
| Iodide of Diethyl-diethene-diammonium | . $[N_2H_2(C_2H_4)_2(C_2H_5)_2]I_2$. |
| Iodide of Triethyl-diethene-diammonium | . $[N_2H(C_2H_4)_2(C_2H_5)_3]I_2$. |
| Iodide of Tetraethyl-diethene-diammonium | . $[N_2(C_2H_4)_2(C_2H_5)_4]I_2$. |

from *Triethene-diamine*:

| | |
|--|------------------------------------|
| Iodide of Diethyl-triethene-diammonium | . $[N_2(C_2H_4)_3(C_2H_5)_2]I_2$. |
|--|------------------------------------|

The diamines also unite directly with water to form ammonium oxides; thus:



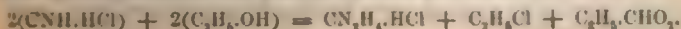
These oxides are very unstable, and give off the water again on mere distillation over potassium hydroxide; when treated with acids, they form diamine-salts, with separation of water.

Methenyl-diamine, $CN_2H_2 = N_2 \left\{ \begin{smallmatrix} (CH)''' \\ H_2 \end{smallmatrix} \right\}$, or *Formylimidamide*,

$\begin{smallmatrix} NH \\ CH \\ NH_2 \end{smallmatrix}$. This base, nearly related to cyanimide or carbodiimide,

$\begin{smallmatrix} NH_2 \\ C \\ NH_2 \end{smallmatrix}$, is known only in combination with acids. The *hydrochloride*,

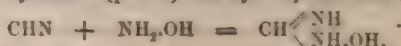
$CN_2H_2.HCl$, is produced together with ethyl chloride and ethyl formate, by heating the compound $CNH.HCl$, formed by direct combination of anhydrous hydrocyanic acid and gaseous hydrochloric acid, with alcohol:



It crystallizes in long needles, soluble in water and alcohol. The base is very unstable, and when separated from the hydrochloric acid, is quickly resolved into ammonia and acetic acid.

Hydroxyl-methenyl-diamine or **Isuret**, $\text{CON}_2\text{H}_4 = \text{CH}$

This base, isomeric with carbamide, is formed by evaporating a solution of hydroxylamine (p. 159) and hydrocyanic acid :

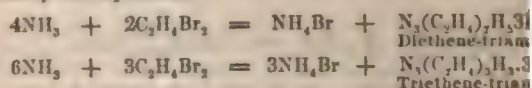


It crystallizes in rhombic prisms resembling carbamide (urea); partial decomposition at $104^\circ\text{--}105^\circ\text{C.}$ ($219.2^\circ\text{--}221^\circ\text{F.}$); has a reaction, and unites with 1 equiv. of acids, forming crystalline salts, which, on heating their solutions, into formic acid, and hydroxylamine. The base itself is also decomposed by boiling solution yielding nitrogen, carbon dioxide, ammonia, guanidine, and biuret.

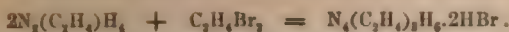
TRIAMINES.

Diethene-triamine, $\text{N}_3 \left\{ \begin{array}{l} \text{C}_2\text{H}_4 \\ \text{C}_2\text{H}_4 \\ \text{H}_2 \end{array} \right.$, and **Triethene-triamine**,

—The hydrobromides of these bases are found amongst the products obtained by heating ethene bromide with ammonia. Their formation is represented by the equations,



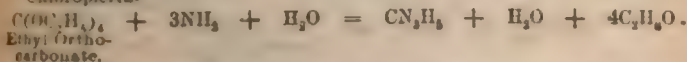
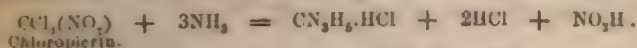
These bases cannot be separated by distillation, on account of the similarity of their boiling points, but their separation is effected by dissolving them into nitro-chlorides, which crystallize with great facility.



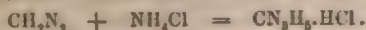
The base, separated from the bromide by silver oxide, is a strongly alkaline liquid, which dries up to a non-crystallizing syrup. The *platinochloride*, $N_4(C_2H_5)_8H_2 \cdot 4HCl \cdot 2PtCl_2$, is a pale yellow amorphous, almost insoluble salt.*

Guanidine, CH_5N_3 , = **Carbotriamine**, $N_3 \left\{ \begin{smallmatrix} C^{IV} \\ H_5 \end{smallmatrix} \right.$, or **Carbimido-**

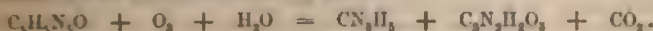
diamide, $C \begin{smallmatrix} \diagup NH_2 \\ NH \\ \diagdown NH_2 \end{smallmatrix}$.—This base is produced: 1. By the action of aqueous ammonia at $150^\circ C.$ ($302^\circ F.$) on chloropierin, or on ethyl orthocarbonate:



2. By heating cyanamide in alcoholic solution with ammonium chloride:



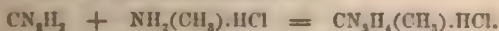
3. Together with parabanic acid, by heating guanine (an alkaloid obtained from guano), with a mixture of hydrochloric acid and potassium chlorate, which exerts an oxidizing action:



Guanidine, separated from its sulphate by baryta-water, forms colorless crystals, easily soluble in water and alcohol: the solution has a powerful alkaline reaction, and absorbs carbonic acid from the air, forming a carbonate, $2CH_5N_3 \cdot H_2CO_3$, which is also alkaline, and crystallizes in square prisms.

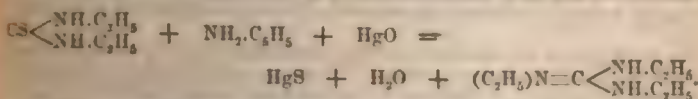
The *nitrate*, $CH_5N_3.NO_2H$, forms large laminae easily soluble in water. The hydrochloride, $CH_5N_3.HCl$, yields a platinochloride, crystallizing in yellow needles.

Alcoholic derivatives of guanidine are formed by reactions analogous to those which yield guanidine itself, especially by heating cyanamide with the hydrochlorides of primary amines: e. g.,



Methyl-guanidine, $CN_2H_4(CH_3)$, is also formed by boiling creatine with water and mercuric oxide. When separated from its hydrochloride by silver oxide it forms a deliquescent crystalline mass, which unites with 1 eq. of acid, forming well-crystallized salts.

Triethyl-guanidine, $CN_2H_4(C_2H_5)_3$, is formed by boiling diethylthiocarbamide and ethylamine in alcoholic solution with mercuric oxide:



The phenyl and tolyl-derivations of guanidine will be described amongst the compounds of the aromatic group; the derivatives containing acid radicals amongst the derivatives of uric acid.

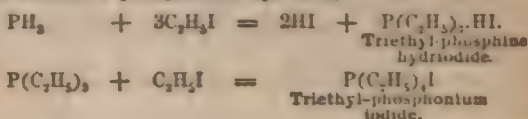
* For further details respecting these higher ethene-bases, see Watts's Dictionary of Chemistry, vol. II. pp. 588-593.

Phosphorus, Arsenic, and Antimony Bases.

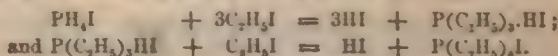
Phosphorus, arsenic, and antimony, being like nitrogen, either trivalent or quinquivalent, are capable of forming compounds analogous to the amines and the ammonium salts.

PHOSPHORUS BASES OR PHOSPHINES.

Tertiary phosphines and phosphonium bases are formed by the action of alcoholic iodides on phosphine, PH_3 ; thus,



or more readily by heating phosphonium iodide, PH_4I (p. 219), to 150° – 180° C. (302° – 356° F.) with alcoholic iodides:

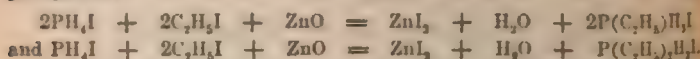


On heating the product with potash-lye, the hydriodide of the tertiary phosphine is decomposed and the base set free, while the iodide of the phosphonium-base remains unaltered.

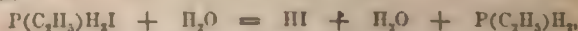
The tertiary phosphines are also formed by distilling the zinc-compounds of the alcohol-radicles with phosphorus trichloride in an atmosphere of hydrogen:



The primary and secondary phosphines are formed by heating the alcoholic iodides with phosphonium iodide to about 150° C. (302° F.) in presence of certain metallic oxides, such as zinc oxide (ordinary zinc-white of commerce), the product being a mixture of the primary and secondary phosphines:



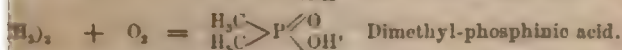
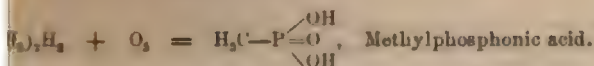
On treating the crystalline product with water, monethyl-phosphine is set free:



while the diethylphosphine salt remains unaltered, but may be decomposed by boiling it with caustic soda, the diethylphosphine being then set free.

The phosphines are colorless, strongly refracting liquids, having an extremely pungent intoxicating odor. They are nearly insoluble in water. In contact with the air, they oxidize rapidly and mostly take fire: hence their preparation must be conducted in an atmosphere of hydrogen. The salts of the primary phosphines are easily decomposed by water, those of the secondary and tertiary phosphines are not.

The primary phosphines are converted by oxidation into phosphonic acids, those of the secondary phosphines into phosphinic acids (p. 555) c. g.,



tertiary phosphines unite directly with 1 atom of oxygen, forming oxides, like $(\text{CH}_3)_3\text{PO}$, and similarly with 1 atom of sulphur, 2 of bromine, iodine, etc., and also with carbon bisulphide.

Following table exhibits the chief distinguishing characters of the primary and ethyl-phosphines:—

| | Boiling Point. | Sp. Gravity. | Hydriodide. | Platino-chloride |
|----------------------|--|---|-----------------------|-----------------------|
| Phosphines:— | | | | |
| H_3 | Gas liquefying at -14°C . (6.8 F.) | .. | Thick crystals. | |
| H_2 | 26°C . (77°F .) | Lighter than water. | .. | Crystallizes well. |
| H | 40°C . (104°F .) | Lighter than water. | .. | |
| Phosphines:— | | | | |
| H_3 | 26°C . (77°F .) | Lighter than water. | Quadrilateral plates. | |
| H_2 | 85°C . (185°F .) | Lighter than water. | .. | Orange-yellow prisms. |
| H | 127°C . (260.6°F .) | 0.812 at 12°C . (53.6°F .) | | Red needles. |

Boiling point of the isopropyl, isobutyl, and isopentyl or amyl phosphines are as follows:—

| | | | |
|--------------------|---|---|---------------------------------------|
| Propyl-phosphines, | $\text{P}(\text{C}_3\text{H}_7)_2\text{H}$ | $\text{P}(\text{C}_3\text{H}_7)_2\text{H}$ | $\text{P}(\text{C}_3\text{H}_7)_3$ |
| B. P. | 41° | 118° | — |
| Butyl-phosphines, | $\text{P}(\text{C}_4\text{H}_9)_2\text{H}$ | $\text{P}(\text{C}_4\text{H}_9)_2\text{H}$ | $\text{P}(\text{C}_4\text{H}_9)_3$ |
| B. P. | 62° | 153° | 215° |
| Amyl-phosphines, | $\text{P}(\text{C}_5\text{H}_{11})_2\text{H}$ | $\text{P}(\text{C}_5\text{H}_{11})_2\text{H}$ | $\text{P}(\text{C}_5\text{H}_{11})_3$ |
| B. P. | $106-107^\circ$ | $210-215^\circ$ | 300° |

ARSENIC BASES.

Triethylarsine, $\text{As}(\text{C}_2\text{H}_5)_3$, is produced by distilling an alloy of arsenic and sodium with ethyl iodide. At the same time, also, there is another body, containing $\text{As}_2(\text{C}_2\text{H}_5)_4$, analogous to arsenodimethyl arsine. Both compounds are liquids of powerful odor; they may be separated by distillation in an atmosphere of carbon dioxide, the triethylarsine passing over last.

Triethylarsine may be obtained pure by a process analogous to that employed for the preparation of triethylphosphine, namely, by distilling arsenic chloride, AsCl_3 , with zinc-ethyl. It is a colorless liquid of most offensive odor, similar to that of arseniethed hydrogen, soluble in water, alcohol, and ether, and boiling at 140°C . (284°F .). Triethylarsine combines directly with oxygen, sulphur, bromine, and iodine, giving rise to a series of compounds containing 2 atoms of bromine or iodine, 1 atom of oxygen, and analogous to the corresponding compounds of triethylphosphine.

Triethylarsine submitted to the action of ethyl iodide yields a crystalline compound, $\text{As}(\text{C}_2\text{H}_5)_4\text{I}$, from which freshly precipitated silver oxide sepa-

rates the corresponding hydroxide, $\text{As}(\text{C}_2\text{H}_5)_3\text{OH}$, a powerfully alkaline substance, similar to the corresponding nitrogen-, phosphorus-, and arsenic-compounds.

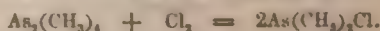
Analogous substances exist in the methyl series. *Trimethylarsonic*, $\text{As}(\text{CH}_3)_3$, is formed, together with *arsendimethyl* or *cacodyl*, $\text{As}_2(\text{CH}_3)_4$, when an alloy of arsenic and sodium is submitted to the action of methyl iodide. It unites with methyl iodide, producing *tetramethylarsonium iodide*, $\text{As}(\text{CH}_3)_4\text{I}$, from which silver oxide separates the hydrate, $\text{As}(\text{CH}_3)_3\text{OH}$. The iodide just mentioned is formed, together with iodide of cacodyl, when cacodyl is acted upon by methyl iodide:



By substituting ethyl iodide for methyl iodide in this reaction, the compound $\text{As}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2\text{I}$ is formed. All these iodides, treated with moist silver oxide, yield the corresponding hydroxides.

Arsendimethyl or Cacodyl, $\text{As}_2(\text{CH}_3)_4$, or $\begin{array}{c} \text{As}(\text{CH}_3)_3 \\ | \\ \text{As}(\text{CH}_3)_3 \end{array}$. — The

arsenic in this compound is trivalent, as in those just described, one unit of equivalence of each of the arsenic atoms being satisfied by combination with the other, just as in the solid hydrogen arsenide, As_2H_4 (p. 399). When, however, the arsendimethyl combines with chlorine or other mono-atomic radicles, the molecule splits into two; thus:



Cacodyl, so called from its repulsive odor, constitutes, together with its products of oxidation, the spontaneously inflammable liquid known as *Cadet's fuming liquid*, or *Alkarsin*. This liquid is prepared by distilling equal weights of potassium acetate and arsenious oxide in a glass retort connected with a condenser and tubulated receiver cooled by ice, a tube being attached to the receiver to carry away the permanently gaseous products to some distance from the experimenter. At the close of the operation, the receiver is found to contain two liquids, besides a quantity of reduced arsenic: the heavier of these is the crude cacodyl; the other consists chiefly of water, acetic acid, and acetone. The gas given off during the distillation is principally carbon dioxide. The crude cacodyl is repeatedly washed by agitation with water previously freed from air by boiling, and afterwards redistilled from potassium hydrate in a vessel filled with pure hydrogen gas. All these operations must be conducted in the open air.

Pure cacodyl is obtained by decomposing the chloride with metallic zinc, dissolving out the zinc chloride with water, and dehydrating the oily liquid with calcium chloride. The strong tendency of cacodyl to take fire in the air, and the extremely poisonous character of its vapor, render it necessary to perform all the distillations in sealed vessels filled with carbon dioxide.

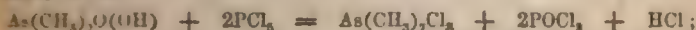
Cacodyl is a colorless, transparent liquid, boiling at 170°C . (338°F .), and crystallizing at 6°C . (42.8°F .) in large transparent prisms. It smokes like alkarsin, and is even more inflammable. At a temperature below redness it is resolved into metallic arsenic and a mixture of 2 vols. methane and 1 vol. ethene: $2\text{As}_2(\text{CH}_3)_4 = \text{As}_4 + 2\text{CH}_4 + \text{C}_2\text{H}_4$.

Cacodyl instantly takes fire when poured out into air or oxygen or chlorine. With very limited access of air it throws off white fumes, passing into oxide and ultimately into cacodylic acid: it combines also directly with sulphur. It can take up 2 atoms of a monad or 1 atom of a dyad element, forming compounds like the chloride, $\text{As}_2(\text{CH}_3)_4\text{Cl}_2 = 2\text{As}(\text{CH}_3)_2\text{Cl}$,

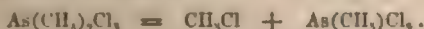
and the oxide, $\text{As}_2(\text{CH}_3)_4\text{O}$, in which the arsenic is trivalent; or again, 6 atoms of a monad or 3 atoms of a dyad element, forming compounds like the trichloride, $\text{As}_2(\text{CH}_3)_4\text{Cl}_6 = 2\text{As}(\text{CH}_3)_2\text{Cl}_3$, in which the arsenic is quinquivalent. These last-mentioned bodies are the most stable of all the cacodyl compounds.

Cacodyl Chloride or Arsen-chlorodimethide, $\text{As}(\text{CH}_3)_2\text{Cl}$, is obtained by distilling alkarsin with strong hydrochloric acid, or better, by mixing the dilute alcoholic solutions of alkarsin and mercuric chloride, distilling the resulting precipitate of cacodylic chloromercurate, $\text{As}_2(\text{CH}_3)_4\text{O} \cdot 2\text{HgCl}_2$, with very strong hydrochloric acid, and digesting the distillate for several days in a sealed bulb apparatus with calcium chloride and quicklime, and finally distilling it in an atmosphere of carbon dioxide.

Cacodyl chloride is a colorless liquid which does not fume in the air, but emits an intensely poisonous vapor. It is heavier than water, insoluble in that liquid and in ether, but easily soluble in alcohol. The boiling point of this compound is a little above 100°C .; its vapor is colorless, spontaneously inflammable in the air, and has a density of 4.56. Dilute nitric acid dissolves the chloride without change; with the concentrated acid ignition and explosion occur. Cacodyl chloride combines with cuprous chloride, forming a white, insoluble, crystalline double salt, containing $\text{As}_2(\text{CH}_3)_4\text{Cl}_2 \cdot \text{Cu}_2\text{Cl}_2$; also with cacodyl oxide. It forms a thick, viscid hydrate, easily dehydrated by calcium chloride. *Cacodyl trichloride*, $\text{As}(\text{CH}_3)_2\text{Cl}_3$, is produced by the action of phosphorus pentachloride on cacodylic acid:



also by the action of chlorine gas on the monochloride. Prepared by the first method, it forms splendid large prismatic crystals, which are instantly decomposed, between 40° and 50°C . (104 – 127°F .), into methyl chloride and arsen-monomethyl chloride:



Cacodyl Iodide, $\text{As}(\text{CH}_3)_2\text{I}$, is a thin, yellowish, heavy liquid, of offensive odor, prepared by distilling alkarsin with strong solution of hydriodic acid. A yellow crystalline oxyiodide is formed at the same time. *Cacodyl bromide and fluoride* have also been obtained.

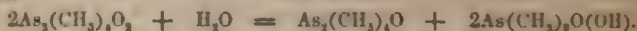
Cacodyl Cyanide, $\text{As}(\text{CH}_3)_2\text{CN}$, is easily formed by distilling alkarsin with strong hydrocyanic acid, or mercuric cyanide. Above 33°C . (91.4°F .), it is a colorless, ethereal liquid, but below that temperature it crystallizes in colorless four-sided prisms, of beautiful diamond lustre. It boils at about 140°C . (284°F .), and is but slightly soluble in water. It takes fire only when heated. The vapor of this substance is most fearfully poisonous: the atmosphere of a room is said to be so far contaminated by the evaporation of a few grains of it as to cause instantaneous numbness of the hands and feet, vertigo, and even unconsciousness.

Cacodyl Oxide, $\text{As}_2(\text{CH}_3)_4\text{O}$, is formed by the slow oxidation of cacodyl. When air is allowed access to an aqueous solution of alkarsin, so slowly that no sensible rise of temperature follows, that body is gradually converted into a thick, syrupy liquid, full of crystals of cacodylic acid. On dissolving this mass in water, and distilling, water having the odor of alkarsin passes over, and afterwards an oily liquid, which is the cacodyl oxide. Impure cacodylic acid remains in the retort.

Cacodyl oxide, purified by rectification from caustic baryta, is a colorless, oily liquid, having a pungent odor, sparingly soluble in water, solidifying at -25°C . (-13°F .), and boiling at 150°C . (302°F .). It strongly resembles alkarsin in odor, in its relations to solvents, and in the greater

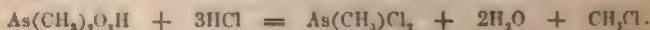
number of its reactions; but it neither fumes in the air, nor takes fire at common temperatures: its vapor mixed with air, and heated to about 88°C . (190.40°F .), explodes with violence. It dissolves in hydrochloric, hydrobromic, and hydriodic acids, forming chloride, bromide, and iodide of cacodyl.

Cacodyl dioride, $\text{As}_2(\text{CH}_3)_4\text{O}_2$, is the thick syrupy liquid produced by the slow oxidation of cacodyl or of alkarsin. It is decomposed by water, and then yields a distillate of cacodyl monoxide, with a residue of cacodylic acid:



Cacodylic or Dimethyl-arsenic Acid, $\begin{matrix} \text{H}_3\text{C} & & \text{O} \\ & \diagdown & / \\ & \text{As} & \\ & / & \diagdown \\ \text{H}_3\text{C} & & \text{OH} \end{matrix}$, also called *Alkarsen*.

—This is the ultimate product of the action of oxygen at a low temperature upon cacodyl or alkarsin in presence of water: it is best prepared by adding mercuric oxide to alkarsin, covered with a layer of water and carefully cooled, until the mixture loses all odor, and afterwards decomposing any mercuric cacodylate that may have been formed, by the cautious addition of more alkarsin. The liquid yields, by evaporation to dryness and solution in alcohol, crystals of cacodylic acid. The sulphide and other compounds of cacodyl yield the same substance on exposure to air. Cacodylic acid forms brilliant, colorless, brittle crystals, which have the form of a modified square prism: it is permanent in dry air, but deliquescent in a moist atmosphere. It is not at all poisonous, though it contains more than 50 per cent. of arsenic. It is very soluble in water and in alcohol, but not in ether: the solution has an acid reaction. When mixed with alkalies and evaporated, it leaves a gummy amorphous mass. With the oxides of silver and mercury, on the other hand, it yields crystallizable compounds. It unites with cacodyl oxide, and forms a variety of combinations with metallic salts. Cacodylic acid is exceedingly stable: it is not affected by red fuming nitric acid, nitromuriatic acid, or even chromic acid in solution: it may be boiled with these substances without the least change. It is deoxidized, however, by phosphorous acid and stannous chloride, yielding cacodyl oxide. Dry hydriodic acid gas decomposes it, with production of water, cacodyl iodide, and free iodine. With dry hydrochloric acid gas, or with the concentrated aqueous acid, cacodylic acid unites directly, forming the compound $\text{As}(\text{CH}_3)_2\text{O}_2\text{H} \cdot \text{HCl}$. But by exposing cacodylic acid for a long time to a stream of hydrochloric acid gas, arsen-monomethyl dichloride is obtained, together with water and methyl chloride:



Phosphorus pentachloride converts cacodylic acid into cacodylic trichloride (p. 653).

Cacodyl Sulphide, $\text{As}_2(\text{CH}_3)_4\text{S}$, is formed by adding barium sulphide to crude cacodyl, or by distilling barium sulphhydrate with cacodyl chloride. It is a transparent liquid which retains its fluidity at -40° , and boils at a temperature considerably above 100°C .

Cacodyl disulphide, $\text{As}_2(\text{CH}_3)_4\text{S}_2$, is formed by the action of sulphur on cacodyl or the monosulphide, or by treating cacodylic acid with sulphuretted hydrogen in a vessel externally cooled. It separates from the solution in large rhombic crystals. Its alcoholic solution yields with various metallic solutions, precipitates consisting of salts of thio-cacodylic acid, $\text{As}(\text{CH}_3)_2\text{S}(\text{SH})$, analogous to cacodylic acid. The lead salt, $\text{As}_2(\text{CH}_3)_4\text{S}_2\text{Pb}$, forms small white crystals.

Arsenmonomethyl, $\text{As}(\text{CH}_3)$.—This radicle, which is not known in the separate state, is either bivalent or quadrivalent. Its dichloride,

$\text{As}(\text{CH}_3)\text{Cl}_2$, is produced either by the decomposition of cacodyl trichloride by heat: $\text{As}(\text{CH}_3)_2\text{Cl}_3 = \text{As}(\text{CH}_3)\text{Cl}_2 + \text{CH}_3\text{Cl}$; or by the prolonged action of hydrochloric acid on cacodylic acid. It is a colorless, heavy mobile liquid, having a strong reducing power; it boils at 133°C . (271.4°F). Its vapor exerts a most violent action on the mucous membranes; on smelling it, the eyes, nose, and whole face swell up, and a peculiar lancinating pain is felt, extending down to the throat. The tetrachloride, $\text{As}(\text{CH}_3)\text{Cl}_4$, is obtained in large crystals by passing chlorine over a mixture of the dichloride and carbon bisulphide cooled to -10°C . (14°F). It is very unstable, decomposing even near 0° into methyl chloride and arsenious chloride, AsCl_3 . There is also a chlorobromide, $\text{As}(\text{CH}_3)\text{ClBr}$, and a di-iodide, $\text{As}(\text{CH}_3)\text{I}_2$.

The oxide, $\text{As}(\text{CH}_3)_2\text{O}$, obtained by decomposing the dichloride with potassium carbonate, forms large cubical crystals, soluble in water, alcohol, and ether, and resolved by distillation with potash into arsenious oxide and cacodyl oxide: $4\text{As}(\text{CH}_3)_2\text{O} = \text{As}_2\text{O}_3 + \text{As}_2(\text{CH}_3)_4\text{O}$.

Arsenmethylic Acid, $\text{As}(\text{CH}_3)\text{O}(\text{OH})_2$, is obtained as a silver-salt by decomposing arsenmethyl dichloride with a slight excess of silver-oxide; and this salt, decomposed by sulphuric acid, yields the acid, which remains on evaporation in the form of a laminated mass. It is bibasic.

Arsenmethyl sulphide, $\text{As}(\text{CH}_3)_2\text{S}$, is obtained as a white mass by passing hydrogen sulphide over the dichloride.

On comparing the combining or equivalent values of the several arsenides of methyl, it will be seen that they all unite with elementary bodies and compound radicals, in such proportions as to form compounds in which the arsenic is either trivalent or quinquivalent, the last-mentioned compounds being by far the most stable. Thus:

Arsenmonomethyl, $\text{As}(\text{CH}_3)$, is bi- and quadri-valent, forming the chlorides $\text{As}(\text{CH}_3)\text{Cl}_2$ and $\text{As}(\text{CH}_3)\text{Cl}_4$.

Arsendimethyl, $\text{As}(\text{CH}_3)_2$, is uni- and tri-valent, forming the chlorides $\text{As}(\text{CH}_3)_2\text{Cl}$ and $\text{As}(\text{CH}_3)_3\text{Cl}_2$.

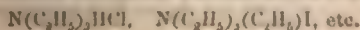
Arsentrimethyl, $\text{As}(\text{CH}_3)_3$, is bivalent only, and forms the chloride $\text{As}(\text{CH}_3)_3\text{Cl}_2$.

Arsenrimethylum, or Tetramethylarsonium, $\text{As}(\text{CH}_3)_4$, is univalent, forming the chloride $\text{As}(\text{CH}_3)_4\text{Cl}$.

ANTIMONY-BASES OR STIBINES.

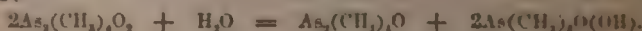
Of these only the tertiary bases and the corresponding stibonium-compounds are known.

Triethylstibine or Stibethyl, $\text{Sb}(\text{C}_2\text{H}_5)_3$, is obtained by distilling ethyl iodide with an alloy of antimony and potassium. It is a transparent, very mobile liquid, having a penetrating odor of onions. It boils at 158°C . (316.4°F). In contact with atmospheric air, it emits a dense white fume, and frequently even takes fire, burning with a white brilliant flame. It is analogous in many of its reactions to triethylamine, but has much more powerful combining tendencies, uniting readily with 2 atoms of chlorine, bromine, or iodine, and 1 atom of oxygen or sulphur, thereby forming compounds in which the antimony is quinquivalent, such as $\text{Sb}(\text{C}_2\text{H}_5)_3\text{Cl}_2$, $\text{Sb}(\text{C}_2\text{H}_5)_3\text{O}$, etc. The same tendency to act as a tervalent radicle is, however, exhibited by triethylamine, which, though it does not unite directly with elementary bodies, can nevertheless take up a molecule of hydrogen chloride, ethyl iodide, etc., likewise producing compounds in which the nitrogen is quinquivalent, e. g.,



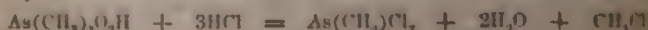
number of its reactions; but it neither fumes in the air, nor takes fire at common temperatures: its vapor mixed with air, and heated to about 300° (190.4° F.), explodes with violence. It dissolves in hydrochloric, hydrobromic, and hydriodic acids, forming chloride, bromide, and iodide of cacodyl.

Cacodyl dioxide, $\text{As}_2(\text{CH}_3)_4\text{O}_2$, is the thick syrupy liquid produced by the slow oxidation of cacodyl or of alkarsin. It is decomposed by water, and then yields a distillate of cacodyl monoxide, with a residue of cacodylic acid:



Cacodylic or Dimethyl-arsenic Acid, $\text{H}_3\text{C} > \text{As} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$, also called *Alkarsen*.

—This is the ultimate product of the action of oxygen at a low temperature upon cacodyl or alkarsin in presence of water: it is best prepared by adding mercuric oxide to alkarsin, covered with a layer of water and carefully cooled, until the mixture loses all odor, and afterwards decomposing any mercuric cacodylate that may have been formed, by the excess addition of more alkarsin. The liquid yields, by evaporation to dryness, a solution in alcohol, crystals of cacodylic acid. The sulphide and other compounds of cacodyl yield the same substance on exposure to air. Cacodylic acid forms brilliant, colorless, brittle crystals, which have the form of a modified square prism: it is permanent in dry air, but deliquescent in a moist atmosphere. It is not at all poisonous, though it contains more than 50 per cent. of arsenic. It is very soluble in water and in alcohol, but not in ether: the solution has an acid reaction. When mixed with alkalies and evaporated, it leaves a gummy amorphous mass. With the oxides of silver and mercury, on the other hand, it yields crystalline compounds. It unites with cacodyl oxide, and forms a variety of combinations with metallic salts. Cacodylic acid is exceedingly stable: it is not affected by red fuming nitric acid, nitromuriatic acid, or even chromic acid in solution: it may be boiled with these substances without the least change. It is decolorized, however, by phosphorous acid and stannous chloride, yielding cacodyl oxide. Dry hydrochloric acid gas decomposes it with production of water, cacodyl iodide, and free iodine. With dry hydrochloric acid gas, or with the concentrated aqueous acid, cacodylic acid unites directly, forming the compound $\text{As}(\text{CH}_3)_3\text{O}_2\text{H} \cdot \text{HCl}$. But by exposing cacodylic acid for a long time to a stream of hydrochloric acid gas, arsen-monomethyl dichloride is obtained, together with water and methyl chloride:



Phosphorus pentachloride converts cacodylic acid into cacodylic trichloride (p. 653).

Cacodyl Sulphide, $\text{As}_2(\text{CH}_3)_4\text{S}$, is formed by adding barium sulphide to crude cacodyl, or by distilling barium sulphhydrate with cacodyl chloride. It is a transparent liquid which retains its fluidity at -40° , and boils at a temperature considerably above 100°C .

Cacodyl disulphide, $\text{As}_2(\text{CH}_3)_4\text{S}_2$, is formed by the action of sulphur on cacodyl or the monosulphide, or by treating cacodylic acid with sulphuretted hydrogen in a vessel externally cooled. It separates from the solution in large rhombic crystals. Its alcoholic solution yields with various metallic solutions, precipitates consisting of salts of thio-cacodylic acid, $\text{As}(\text{CH}_3)_3\text{S}(\text{SH})$, analogous to cacodylic acid. The lead salt $\text{As}_2(\text{CH}_3)_4\text{S}_2\text{Pb}$, forms small white crystals.

Arsenmonomethyl, $\text{AsO}(\text{H})$.—This radical, which is not known in the separate state, is either bivalent or quadrivalent. Its derivatives

Cl_3 , is produced either by the decomposition of cacodyl trichloride $\text{As}(\text{CH}_3)_2\text{Cl}_3 = \text{As}(\text{CH}_3)\text{Cl}_2 + \text{CH}_3\text{Cl}$; or by the prolonged action of hydrochloric acid on cacodylic acid. It is a colorless, heavy mobile liquid, having a strong reducing power: it boils at 133°C . (271.4°F). It exerts a most violent action on the mucous membranes; on the face, the eyes, nose, and whole face swell up, and a peculiar lancinating pain is felt, extending down to the throat. The tetrachloride, Cl_4 , is obtained in large crystals by passing chlorine over a mixture of the dichloride and carbon bisulphide cooled to -100°C . (140°F). It is unstable, decomposing even near 0° into methyl chloride and dichloride, AsCl_3 . There is also a chlorobromide, $\text{As}(\text{CH}_3)\text{ClBr}$, and an iodide, $\text{As}(\text{CH}_3)\text{I}_2$.

The trioxide, $\text{As}(\text{CH}_3)_3\text{O}$, obtained by decomposing the dichloride with potassium carbonate, forms large cubical crystals, soluble in water, alcohol, ether, and resolved by distillation with potash into arsenious oxide and methyl oxide: $4\text{As}(\text{CH}_3)_3\text{O} = \text{As}_2\text{O}_3 + \text{As}_2(\text{CH}_3)_4\text{O}$.

Methyllic Acid, $\text{As}(\text{CH}_3)_3\text{O}(\text{OH})_2$, is obtained as a silver-salt by decomposing arsenomethyl dichloride with a slight excess of silver-oxide; the silver salt, decomposed by sulphuric acid, yields the acid, which resists evaporation in the form of a laminated mass. It is bibasic.

Methyl sulphide, $\text{As}(\text{CH}_3)_2\text{S}$, is obtained as a white mass by passing hydrogen sulphide over the dichloride.

Comparing the combining or equivalent values of the several arsenomethyls, it will be seen that they all unite with elementary bodies in round radicles, in such proportions as to form compounds in which antimony is either trivalent or quinquivalent, the last-mentioned combining being by far the most stable. Thus:

Monomethyl, $\text{As}(\text{CH}_3)$, is bi- and quadri-valent, forming the chlorides Cl_2 and Cl_4 .

Dimethyl, $\text{As}(\text{CH}_3)_2$, is uni- and tri-valent, forming the chlorides Cl and $\text{As}(\text{CH}_3)_2\text{Cl}_3$.

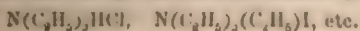
Trimethyl, $\text{As}(\text{CH}_3)_3$, is bivalent only, and forms the chloride Cl_2 .

Tetramethyl, or Tetramethylarsonium, $\text{As}(\text{CH}_3)_4$, is univalent, forming the chloride $\text{As}(\text{CH}_3)_4\text{Cl}$.

ANTIMONY-BASES OR STIBINES.

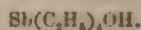
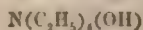
Only the tertiary bases and the corresponding stibonium-compounds are known.

Triethylstibine or Stibethyl, $\text{Sb}(\text{C}_2\text{H}_5)_3$, is obtained by distilling triethyl iodide with an alloy of antimony and potassium. It is a colorless, very mobile liquid, having a penetrating odor of onions. It boils at 158°C . (316.4°F). In contact with atmospheric air, it emits a white fume, and frequently even takes fire, burning with a white flame. It is analogous in many of its reactions to triethylamine, but with much more powerful combining tendencies, uniting readily with oxygen, of chlorine, bromine, or iodine, and 1 atom of oxygen or sulphur, forming compounds in which the antimony is quinquivalent, $\text{Sb}(\text{C}_2\text{H}_5)_3\text{Cl}_2$, $\text{Sb}(\text{C}_2\text{H}_5)_3\text{O}$, etc. The same tendency to act as a radical is, however, exhibited by triethylamine, which, though it does not unite directly with elementary bodies, can nevertheless take up 1 atom of hydrogen chloride, ethyl iodide, etc., likewise producing compounds in which the nitrogen is quinquivalent, e. g.,



Stibethyl oxide, $\text{Sb}(\text{C}_2\text{H}_5)_3\text{O}$, forms a viscid, transparent, bitter, non-poisonous mass, soluble in water and alcohol; not volatile without decomposition. Treated with acids, it forms crystallizable salts containing 2 molecules of a monatomic or 1 molecule of a diatomic acid radicle, e.g., $\text{Sb}(\text{C}_2\text{H}_5)_3(\text{NO}_3)_2$, $\text{Sb}(\text{C}_2\text{H}_5)_3\text{SO}_4$, etc. The *sulphide*, $\text{Sb}(\text{C}_2\text{H}_5)_3\text{S}$, forms beautiful crystals of silvery lustre, soluble in water and alcohol. Their taste is bitter, and their odor similar to that of mercaptan. The solution of this compound exhibits the deportment of an alkaline sulphide: it precipitates metals from their solutions as sulphides, a soluble salt of stibethyl being formed at the same time. This deportment, indeed, affords the simplest means of preparing the salts of stibethyl. The *chloride*, $\text{Sb}(\text{C}_2\text{H}_5)_3\text{Cl}$, is a colorless liquid, having the odor of turpentine oil. The *iodide*, $\text{Sb}(\text{C}_2\text{H}_5)_3\text{I}$, forms colorless needles of intensely bitter taste.

The analogy of triethylstibine to triethylamine is best exhibited in its deportment with ethyl iodide. The two substances combine, forming tetraethylstibonium iodide, $\text{Sb}(\text{C}_2\text{H}_5)_4\text{I}$, from which silver oxide separates a powerful alkaline base analogous to tetraethylammonium hydroxide:



A series of analogous substances exists in the methyl series. They have been examined by Landolt, who has described several of their compounds, and separated the methyl-antimony-base analogous to tetramethylammonium hydrate.

The *iodide*, $\text{Sb}(\text{CH}_3)_3\text{I}$, produced by the action of methyl iodide upon trimethylstibine, $\text{Sb}(\text{CH}_3)_3$, crystallizes in white six-sided tables, which are easily soluble in water and alcohol, and slightly soluble in ether. It has a very bitter taste, and is decomposed by the action of heat. When treated with silver oxide, it yields a powerfully alkaline solution, exhibiting all the properties of potash, from which, on evaporation, a white crystalline mass, the *hydroxide of tetramethylstibonium*, $\text{Sb}(\text{CH}_3)_4(\text{OH})$, crystallizes. This compound forms an acid sulphate, $\text{Sb}(\text{CH}_3)_4\text{SO}_4\text{H}$, which crystallizes in tables.

Bismethyl or Triethylbismuthine, $\text{Bi}(\text{C}_2\text{H}_5)_3$, analogous in composition to triethylstibine and triethylarsine, is formed by the action of ethyl iodide on an alloy of bismuth and potassium, and is extracted from the residue by ether. It is a yellow liquid of specific gravity 1.52, has a most nauseous odor, and emits vapors which take fire in contact with the air. It unites with oxygen, chlorine, bromine, iodine, and nitric acid.

DIATOMIC BASES OF THE PHOSPHORUS AND ARSENIC SERIES.

The action of ethene bromide on triethylphosphine gives rise to the formation of two crystalline bromides, according to the proportions in which the substances are brought in contact. These bromides are $\text{C}_6\text{H}_{15}\text{PBr}_1 = (\text{C}_2\text{H}_5)_3\text{P} + \text{C}_2\text{H}_4\text{Br}_2$ and $\text{C}_{11}\text{H}_{24}\text{P}_2\text{Br}_2 = 2(\text{C}_2\text{H}_5)_3\text{P} + \text{C}_2\text{H}_4\text{Br}_2$. The first of these compounds is the bromide of a phosphonium in which 3 atoms of hydrogen are replaced by ethyl and 1 atom by the univalent radicle bromethyl, $\text{C}_2\text{H}_4\text{Br}$, namely, $[(\text{C}_2\text{H}_4\text{Br})(\text{C}_2\text{H}_5)_2\text{P}]\text{Br}$. Half the bromine in this salt is unaffected by the action of silver-salts; it may accordingly be designated as *bromide of bromethyl-triethyl-phosphonium*. Numerous salts of this compound are known, but the free base cannot be obtained, since silver oxide eliminates the latent bromine, giving rise to the formation of a base containing $[(\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_5)_2\text{P}]\text{OH}$. The second compound is the dibromide

of *ethene-hexethyl-diphosphonium* $[(C_2H_4)(C_2H_5)_6P_2]Br_2$. This radicle, analogous to diammonium, N_2H_5 , forms a series of very stable and beautiful salts, especially an iodide, which is difficultly soluble in water. In all these salts the base, which is composed of 1 atom of ethene, 6 atoms of ethyl, and 2 atoms of phosphorus, is united with 2 equivalents of univalent acid radicle; the platinum-salt contains $(C_2H_4)(C_2H_5)_6P_2Br.PtCl_4$. The very caustic and stable base has the composition $[(C_2H_4)(C_2H_5)_6P_2](OH)_2$.

The dibromide of ethene-hexethyl-diphosphonium may be formed by the action of triethylphosphine upon the brominated bromide which has been mentioned as the first product of the action of ethene dibromide upon triethylphosphine: $C_6H_{18}PBr_2 \cdot (C_2H_5)_3P = C_{14}H_{34}P_2Br_2$. If the triethylphosphine be replaced in this process by ammonia or by monamines in general, or by monarsines, an almost unlimited series of diatomic salts may be formed, in which phosphorus and nitrogen or phosphorus and arsenic are associated.

Thus the action of ammonia, of ethylamine, and triethylarsine, gives rise respectively to the following compounds:

| | |
|--|-------------------------------------|
| Dibromide of Ethene-triethyl-phosphammonium | } $[(C_2H_4)(C_2H_5)_3H_2PN]Br_2$. |
| Dibromide of Ethene-tetrethyl-phosphammonium | |
| Dibromide of Ethene-hexethyl-phospharsonium | } $[(C_2H_4)(C_2H_5)_6PA_2]Br_2$. |
| | |

Treated with silver oxide these bromides yield the very caustic diatomic bases—

| | |
|--|---------------------------------------|
| Hydroxide of Ethene-triethyl-phosphammonium | } $[(C_2H_4)(C_2H_5)_3H_2PN](OH)_2$. |
| Hydroxide of Ethene-tetrethyl-phosphammonium | |
| Hydroxide of Ethene-hexethyl-phospharsonium | } $[(C_2H_4)(C_2H_5)_6PA_2](OH)_2$. |
| | |

The arsenic bases, when submitted to the action of ethene dibromide, give rise to perfectly analogous results. The limits of this Manual will not permit us to examine these compounds in detail.

ORGANO-BORON COMPOUNDS.

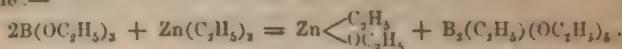
Boric Triethide, or Borethyl, $B(C_2H_5)_3$, discovered by Frankland, is obtained, together with zinc-ethoxide, by treating triethyllic borate with zinc-ethide:—



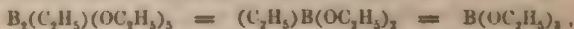
It is a colorless, mobile liquid, having a pungent odor, irritating the eyes, of sp. gr. 0.696 at 23° C. (73.4° F.), and boiling at 95° C. (203° F.). Borethyl is insoluble in water, but very slowly decomposed when left in prolonged contact with it. When exposed to the air it takes fire, burning with a beautiful green and somewhat smoky flame. It combines with ammonia, forming the compound $NH_3 \cdot B(C_2H_5)_3$. By the gradual action of dry air, and ultimately of dry oxygen, borethyl is converted into the di-ethyllic ether of ethylboric acid, $(C_2H_5)_2B \begin{smallmatrix} \nearrow OC_2H_5 \\ \searrow OC_2H_5 \end{smallmatrix}$, a liquid boiling, with

partial decomposition, between 95° and 115° C. (203° and 239° F.), but distilling unchanged under reduced pressure. In contact with water this liquid is immediately transformed into ethylboric acid, $(C_2H_5)_3B(OH)_3$.

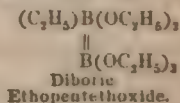
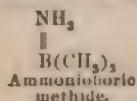
*Diboric Ethopentethoxide** (or Ethopentethylate), $H_2(C_2H_5)_4(OC_2H_5)_2$, is formed by heating 2 molecules of boric ether with 1 molecule of zinc ethide:—



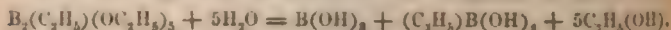
It is a colorless, mobile liquid, boiling at about 120° C. (248° F.), and condensing unchanged. Its vapor-density, taken between 114° and 120° C. (237.2° and 248° F.), is 69 ($H=1$), which represents a four-volume condensation, indicating that the compound, in passing from the liquid to the gaseous state, is broken up into diethylic ethylborate and boric ether:—



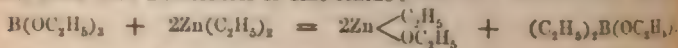
just as sal-ammoniac, NH_4Cl , is resolved by heat into NH_3 and HCl , which together occupy four volumes of vapor (p. 230). A similar deportment is exhibited by ammonioboric methide, $NH_3 \cdot B(CH_3)_3$, which is resolved by heat into NH_3 and $B(CH_3)_3$, the mixed vapor resulting from the decomposition having also a four-volume condensation. These results render it probable that the compounds under consideration have a constitution analogous to that of the ammonium salts, and that boron, though generally triadic, may, like nitrogen, enter into combination also as a pentad. On this view the constitution of ammonioboric methide and diboric ethopentethoxide may be represented by the following formulæ:—



In contact with water, diboric ethopentethoxide is immediately decomposed into boric acid, ethyl-boric acid, and alcohol:—



Boric Diethylethoxide, $(C_2H_5)_2B(OC_2H_5)_2$, is produced by boiling boric ether with 2 molecules of zinc ethide:—



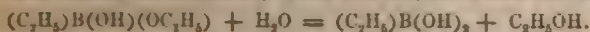
When purified by distillation in an atmosphere of carbon dioxide, it is a colorless, mobile pungent liquid boiling at 102° C. (215.6° F.), and having at 135.5° C. (275.9° F.) a vapor-density of 56.5 ($H=1$), indicating a normal two-volume condensation. It takes fire in the air, and burns with a green flame. Exposed to dry air and then to oxygen, it oxidizes to boric ethyldiethoxide, $(C_2H_5)_3B(OC_2H_5)_2$.

Boric Diethylethoxide, $(C_2H_5)_2B(OH)_2$, formed by agitating boric diethyl-ethoxide with water, is a spontaneously inflammable ethereal liquid, resembling boric ethide, and decomposing when distilled.

Boric Ethyl-hydroethoxide, $(C_2H_5)_2B\begin{smallmatrix} OC_2H_5 \\ \diagup \\ OH \end{smallmatrix}$, is formed by exposing the last compound in a cooled vessel to a slow current of dry air. It is liquid at ordinary temperatures, but solidifies below 8° C. (46.4° F.)

* This and the following compounds have quite recently been discovered by Frankland (Proc. Roy. Soc. 1870, vol. xxy, p. 165).

to a white crystalline body smelling like borethide, and having a pungent taste. It is rapidly decomposed by water into ethylboric acid and alcohol:



It is not spontaneously inflammable, and cannot be distilled under ordinary atmospheric pressure without decomposition.

Boric Trimethide, or **Bor-methyl**, $B(CH_3)_3$, obtained like the ethyl-compound, is a colorless gas, which condenses to a liquid at low temperatures. It unites with ammonia, forming the compound $H_2N \equiv B(CH_3)_3$.

ORGANO-SILICON COMPOUNDS.

Silicon is a tetrad element, and forms with alcohol-radicles compounds bearing a very close analogy to the hydrocarbons.

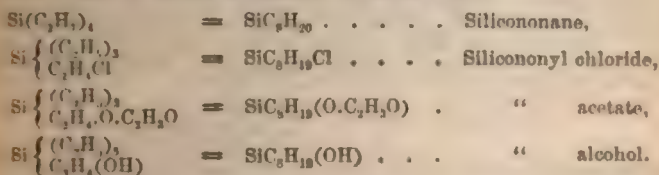
Silicic Tetramethide, $Si(CH_3)_4$, is produced by heating silicon tetrachloride with zinc methide:—



It is a mobile liquid, which boils at $30^\circ C.$ ($86^\circ F.$), is not decomposed by water, and reacts generally like a hydrocarbon, viz., tetramethyl-methane.

Silicic Tetrethide, $Si(C_2H_5)_4$, prepared like the methyl-compound, is a liquid boiling at $153^\circ C.$ ($307.4^\circ F.$). With chlorine it yields the monochlorinated derivative, $Si \left\{ \begin{smallmatrix} (C_2H_5)_3 \\ C_2H_4Cl \end{smallmatrix} \right.$, which boils at $185^\circ C.$ ($365^\circ F.$) and reacts exactly like the chloride of a hydrocarbon, being converted by potassium acetate into the acetic ether, $Si \left\{ \begin{smallmatrix} (C_2H_5)_3 \\ C_2H_4(OC_2H_3O) \end{smallmatrix} \right.$, which boils at $211^\circ C.$ ($411.8^\circ F.$), and is decomposed by alkalis into acetic acid, and an alcohol having the composition $Si \left\{ \begin{smallmatrix} (C_2H_5)_3 \\ C_2H_4OH \end{smallmatrix} \right.$. This alcohol is a liquid insoluble in water, and boiling at $190^\circ C.$ ($374^\circ F.$).

Silicic tetrethide and its derivatives may be regarded as *nonyl-compounds* in which 1 atom of carbon is replaced by silicon; thus:



Ethylated Silicic Ethers.—When normal silicic ether, $Si(OC_2H_5)_4$, is heated with zinc-ethyl and sodium, one or all of the ethoxyl-groups are replaced by ethyl, the product being a mixture of mono-, di-, and triethylated silicic ethers, and silicic tetrethide, which may be separated by fractional distillation.

Triethylsilicic ether, $(C_2H_5)_3Si(OC_2H_5)$, or **Silicoheptyl-ethyl oxide**, $SiC_7H_{17}O.C_2H_5$, is a liquid, of specific gravity 0.841 at $0^\circ C.$, boiling at

153° C. (307.4° F.), insoluble in water. Treated with acetic anhydride, it yields an acetic ether, convertible by the action of potash into triethyl silicon-hydroxide, $(C_2H_5)_3Si(OH)$, which is a tertiary silicic alcohol, analogous to triethyl-carbinol, and is hence called triethyl-silicic alcohol. It is a colorless, oily liquid, smelling like camphor, insoluble in water, boiling at 154° C. (309.2° F.).

Diethylsilicic ether, $(C_2H_5)_2Si(OC_2H_5)_2$, is a fragrant liquid, insoluble in water, boiling at 155.8° C. (312.4° F.), and having a specific gravity of 0.875 at 0° C. When heated with acetyl chloride, it yields the compounds $(C_2H_5)_2Si(OC_2H_5)Cl$ and $(C_2H_5)_2SiCl_2$. The latter is a fuming liquid, boiling at 148° C. (298.4° F.), and converted by water into diethylsilicic oxide $(C_2H_5)_2SiO$, analogous to diethyl ketone, $(C_2H_5)_2CO$.

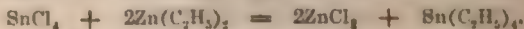
Monethyl silicic ether, $(C_2H_5)Si(OC_2H_5)_3$, is a liquid smelling like camphor, boiling at 159° C. (318.2° F.), slowly decomposed by water. Heated with acetyl chloride, it yields ethylsilicon trichloride, $(C_2H_5)SiCl_3$, a strongly fuming liquid which boils at 100°, and is converted by water into ethylsilicic or silicopropionic acid, $C_2H_5SiO.OH$. This acid is a white amorphous powder, which moulders away when heated in the air, and dissolves in aqueous potash and soda, forming silico-propionates.

ORGANO-METALLIC COMPOUNDS.

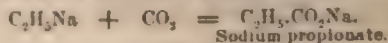
The name is especially applied to compounds of alcohol-radicles with metals not belonging to the pentad group. Those containing the more basic metals, such as zinc, are formed by the direct action of the metals, or better, of their sodium alloys, on the alcoholic iodides: e. g.,



Those containing the less basic metals (tin, lead, etc.) are produced by the action of organo-zinc or mercury-compounds on metallic chlorides: e. g.,



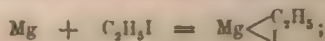
Potassium Ethide, C_2H_5K , and **Sodium Ethide**, C_2H_5Na , are known only in combination or mixture with zinc ethide, in which state they are obtained by the action of potassium or sodium on zinc ethide. These compounds and their homologues, discovered by Wanklyn, have played an important part in chemical synthesis. They absorb carbon-dioxide, producing salts of the fatty acids:



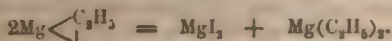
By the action of carbon monoxide they are converted into ketones:



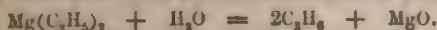
Magnesium Ethide, $Mg(C_2H_5)_2$.—When ethyl iodide is heated with magnesium filings in a vessel from which the air is excluded, magnesium ethiodide is formed in the first instance according to the equation:



and this compound, when heated, is resolved into iodide and ethide :



Magnesium ethide is a liquid which takes fire spontaneously in the air, and is rapidly decomposed by water, with formation of ethane :

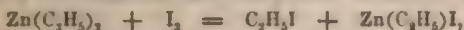


Zinc Ethide or **Zinc-ethyl**, $\text{Zn}(\text{C}_2\text{H}_5)_2$, is formed by heating ethyl iodide with zinc in a sealed glass tube, or for larger quantities, in a strong and well-closed copper cylinder. The reaction takes place in the same manner as with magnesium, zinc ethiodide, $\text{Zn}(\text{C}_2\text{H}_5)\text{I}$, being formed in the first instance as a white crystalline mass, which, when distilled in an atmosphere of hydrogen, is resolved into zinc-iodide and zinc-ethide, the latter distilling over.

Zinc-ethide is a mobile and very volatile disagreeable-smelling liquid, having a specific gravity of 1.182, and boiling at 118°C . (244.4°F .). It takes fire instantly on coming in contact with the air, diffusing white fumes of zinc oxide. Water decomposes it violently, with formation of zinc hydride, and evolution of ethane :



When gradually mixed with dry oxygen, it passes through two stages of oxidation, yielding first zinc-ethyl-ethoxide, $\text{Zn} \left\{ \begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{OC}_2\text{H}_5 \end{array} \right.$, and finally zinc-ethoxide, $\text{Zn}(\text{OC}_2\text{H}_5)_2$. With iodine and other halogens, the reaction also takes place by two stages, but consists in the successive substitution of the halogen for the ethyl; thus :



and



Zinc Methide, $\text{Zn}(\text{CH}_3)_2$, prepared in like manner, is a mobile spontaneously inflammable liquid, which boils at 46°C . (114.8°F .), and resembles the ethyl compound in all its reactions.

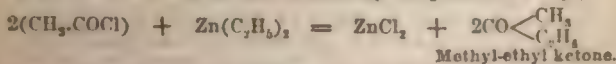
Zinc Isopropide, $\text{Zn}(\text{C}_3\text{H}_7)_2$, boils at 146°C . (294.8°F .). **Zinc isopentide**, or **Zinc amylide**, $\text{Zn}(\text{C}_5\text{H}_{11})_2$, boils at 220°C . (428°F .), and burns strongly in the air, but does not take fire spontaneously.

These organo-zinc compounds, discovered by Frankland, are very important reagents in organic synthesis, serving to effect the substitution of the positive radicle ethyl, etc., for chlorine, iodine, and other negative elements, and thus enabling us to build up carbon-compounds from others lower in the scale. With carbon oxychloride (phosgene) they form ketones :



Acetone.

also with the chlorides of acid radicles at ordinary temperatures : e. g.,



Methyl-ethyl ketone.

They also serve, as already mentioned, for the preparation of other organo-metallic bodies : e. g.,

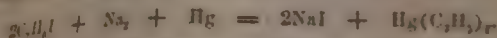


153° C.
it yields
siliceous
analog
It is
boiled

It
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of
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lie
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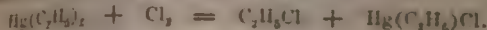
As the reaction of the zinc-compounds, with formation of zinc-ethide, is analogous to that of the zinc-ethide, forming a crystalline compound, the reaction of zinc-ethide with water and carbon dioxide, is comparable to that of zinc-ethide with acetic acid, $C_2H_3N_2O_2H$, the structure of which is not yet satisfactorily made out.

Mercuric Ethide. $Hg(C_2H_5)_2$.—This compound is formed by the action of zinc-ethide on zinc-ethide, but it is more easily prepared by the action of sodium-amalgam on ethyl iodide in presence of acetic ether.

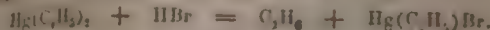


The acetic ether takes no part in the reaction; nevertheless its presence appears to be essential.

Mercuric ethide is a transparent colorless liquid, boiling at 159° C. (318° F.), and having a sp. gr. of 2.44. It burns with a smoky flame, giving off a large quantity of mercurial vapor. Chlorine, bromine, and iodine remove one equivalent of ethyl from this compound, and take its place, forming mercuric ethylchloride, etc.; thus:



A similar action is exerted by acids, e. g., by hydrobromic acid, the products being ethane and mercuric bromethide:

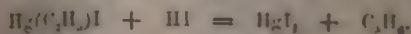


The ethylchloride or bromethide is converted by water into mercuric ethylhydrate, $Hg(C_2H_5)(OH)$. Mercuric ethide serves for the preparation of several other organo-metallic bodies.

Mercuric Methide. $Hg(CH_3)_2$, prepared by similar processes, is a liquid slightly soluble in water, boiling at 95° C. (203° F.), and having a specific gravity of 3.069.

Mercuric Isopentide or Amylide. $Hg(C_5H_{11})_2$ is a thick liquid of specific gravity 1.66, decomposed by distillation.

Mercuric Allylhydride. $Hg\left(C_3H_5\right)_2$, produced by agitating allyl iodide with mercury, crystallizes from alcohol in silvery laminae, melting at 11° C. (52° F.). With hydrogen iodide, it yields mercuric iodide and propene:



Aluminium Methide. $Al(CH_3)_3$, or $Al_2(CH_3)_6$. This compound, discovered by Buckton and Odling, is formed by heating mercuric methide with aluminium. It is a mobile liquid, which crystallizes at a high altitude, and boils at 130° C. (266° F.). At and above 220° C. (428° F.) the density of its vapor, compared with that of air, is 2.8, which is near the theoretical density calculated for the formula $Al(CH_3)_3$, namely, 2. This seems to show that the true formula of the compound is $Al(CH_3)_3$, and not $Al_2(CH_3)_6$, and, consequently, that aluminium is a triad, not a hexad (p. 240). At temperatures near the boiling point, however, the vapor density becomes 4.1, approximating to the theoretical density calculated for the formula, $Al_2(CH_3)_6$.

Aluminium Ethide. $Al(C_2H_5)_3$, or $Al_2(C_2H_5)_6$, resembles the mercuric compound. It boils at 184° C. (361.2° F.), and its vapor likewise exhibits

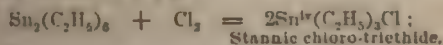
temperatures considerably above its boiling point, a density nearly equal required by the formula $\text{Al}(\text{C}_2\text{H}_5)_3$, for a two-volume condensa-

Compounds.—Tin forms two ethyl-compounds, $\text{Sn}(\text{C}_2\text{H}_5)_2$, $(\text{C}_2\text{H}_5)_4\text{Sn}$, analogous to stannous and stannic chloride; also a stannous ethide, $\text{Sn}_2(\text{C}_2\text{H}_5)_6$, analogous in constitution to ethane, C_2H_6 . Ethide is a saturated compound, but the other two are unsaturated, capable of uniting with chlorine, bromine, oxygen, and acid radicals being thereby converted into compounds of the stannic type.

Stannous Ethide, $\text{Sn}(\text{C}_2\text{H}_5)_2$.—When ethyl iodide and tin-foil are heated in a sealed glass tube to about 150° or 180°C . (302 – 356°F .), diethide, $\text{Sn}(\text{C}_2\text{H}_5)_2$, is produced, crystallizing in colorless needles. The compound is obtained when tin and ethyl iodide are exposed to rays of the sun concentrated by a concave mirror. The reaction is considerably facilitated if the tin be alloyed with one-tenth of its weight of zinc. This iodide is decomposed by sodium or zinc, which abstracts the iodine and leaves stannous ethide in the form of a thick, oily liquid, insoluble in water, having the sp. gr. 1.558, and decomposed by distillation. Stannous ethide combines directly with 2 atoms of chlorine, iodine, bromine, forming stannic chloroethide, $\text{Sn}^{IV}(\text{C}_2\text{H}_5)_2\text{Cl}_2$, etc. Exposed to air, it absorbs oxygen, and is converted into stannic oxethide, H_2SnO_3 , a whitish, tasteless, inodorous powder, which when treated with oxygen-acids, yields well-crystallized stannic salts, such as $\text{K}_2(\text{NO}_3)_2$, $\text{Sn}(\text{C}_2\text{H}_5)_2\text{SO}_4$, etc.

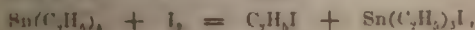
Stannoso-stannic Ethide, $\text{Sn}_2(\text{C}_2\text{H}_5)_6$, is always produced in small quantity when stannous ethide is prepared by the methods above mentioned.

It is readily obtained in the free state by digesting an alloy of 1 part of sodium and 5 parts of tin with ethyl iodide, exhausting the mass with ether, evaporating the ethereal solution, and exhausting the residue with alcohol. The stannoso-stannic ethide, being insoluble in that liquid, remains behind. It is a yellow oil, boiling at 180°C . (356°F .), and reacting directly with chlorine, bromine, and iodine to form two molecules of a stannic compound; e. g.:



It combines with oxygen, forming distannic oxy-hexethide, $\text{Sn}_2^{IV}(\text{C}_2\text{H}_5)_6\text{O}$. This is, however, best obtained by distilling stannic oxy-diethide, H_2SnO_3 (above described), with potash. It is an oily liquid, soluble in alcohol, ether, and water; the aqueous solution has a strong alkaline reaction. It is easily acted upon by oxygen-acids, yielding the corresponding sulphate, $\text{Sn}_2(\text{C}_2\text{H}_5)_6\text{SO}_4$, etc.

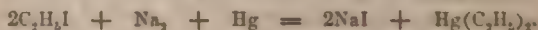
Stannic Ethane, $\text{Sn}^{IV}(\text{C}_2\text{H}_5)_4$, is produced by the action of zinc ethide on stannic chloride; also by the distillation of stannous ethide: $2\text{Sn}(\text{C}_2\text{H}_5)_2 = \text{Sn}(\text{C}_2\text{H}_5)_4$. It is a colorless, nearly odorless liquid, of sp. gr. 1.011, boiling at 181°C . (257.8°F .), and very inflammable, burning with a very luminous flame. When treated with chlorine, bromine, etc., or acids, it forms substitution-products: thus, with iodine, it splits up into ethyl iodide and stannic iodotriethide:



or, with hydrochloric acid, it yields ethane and stannic chlorotriethide, $\text{Sn}(\text{C}_2\text{H}_5)_3\text{Cl} + \text{HCl} = \text{C}_2\text{H}_6 + \text{Sn}(\text{C}_2\text{H}_5)_3\text{Cl}$.

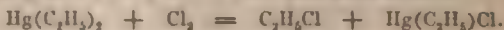
Sulphur dioxide is absorbed by these zinc-compounds, with formation of the zinc salts of methyl- and ethyl-dithionic or sulphinic acids (p. 554). *Nitrogen dioxide* dissolves in zinc-ethide, forming a crystalline compound, which, by the action of water and carbon dioxide, is converted into the zinc salt of dinitroethylic acid, $C_2H_3.N_2O_2H$, the structure of which has not yet been satisfactorily made out.

Mercuric Ethide, $Hg(C_2H_5)_2$.—This compound is formed by the action of mercuric chloride on zinc ethide, but it is more easily prepared by the action of sodium-amalgam on ethyl iodide in presence of acetic ether:

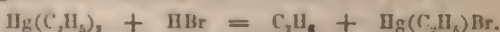


The acetic ether takes no part in the reaction; nevertheless its presence appears to be essential.

Mercuric ethide is a transparent colorless liquid, boiling at $159^\circ C.$ ($318.2^\circ F.$), and having a sp. gr. of 2.44. It burns with a smoky flame, giving off a large quantity of mercurial vapor. Chlorine, bromine, and iodine remove one equivalent of ethyl from this compound, and take its place, forming mercuric chloroethide, etc.; thus:



A similar action is exerted by acids, *e. g.*, by hydrobromic acid, the products being ethane and mercuric bromethide:

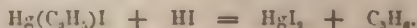


The chloroethide or bromethide is converted by water into mercuric ethyl-hydrate, $Hg(C_2H_5)(OH)$. Mercuric ethide serves for the preparation of several other organo-metallic bodies.

Mercuric Methide, $Hg(CH_3)_2$, prepared by similar processes, is a liquid slightly soluble in water, boiling at $95^\circ C.$ ($203^\circ F.$), and having a specific gravity of 3.069.

Mercuric Isopentide or Amylide, $Hg(C_4H_9)_2$, is a thick liquid, of specific gravity 1.66, decomposed by distillation.

Mercuric Allyl iodide, $Hg\langle C_3H_5 \rangle_2$, produced by agitating allyl iodide with mercury, crystallizes from alcohol in silvery laminae, melting at $135^\circ C.$ ($275^\circ F.$). With hydrogen iodide, it yields mercuric iodide and propene:



Aluminium Methide, $Al(CH_3)_3$, or $Al_2(CH_3)_6$. This compound, discovered by Buckton and Odling, is formed by heating mercuric methide with aluminium. It is a mobile liquid, which crystallizes at a little above 0° , and boils at $130^\circ C.$ ($266^\circ F.$). At and above $220^\circ C.$ ($428^\circ F.$) the density of its vapor, compared with that of air, is 2.8, which is near to the theoretical density calculated for the formula $Al(CH_3)_3$, namely, 2.5. This seems to show that the true formula of the compound is $Al(CH_3)_3$, and not $Al_2(CH_3)_6$, and, consequently, that aluminium is a triad, not a tetrad (p. 246). At temperatures near the boiling point, however, the vapor-density becomes 4.4, approximating to the theoretical density calculated for the formula, $Al_2(CH_3)_6$.

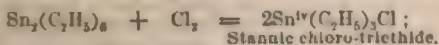
Aluminium Ethide, $Al(C_2H_5)_3$, or $Al_2(C_2H_5)_6$, resembles the methyl compound. It boils at $194^\circ C.$ ($381.2^\circ F.$), and its vapor likewise exhibits,

at temperatures considerably above its boiling point, a density nearly equal to that required by the formula $\text{Al}(\text{C}_2\text{H}_5)_3$, for a two-volume condensation.

Tin Compounds.—Tin forms two ethyl-compounds, $\text{Sn}(\text{C}_2\text{H}_5)_2$, and $\text{Sn}(\text{C}_2\text{H}_5)_4$, analogous to stannous and stannic chloride; also a stannous-stannic ethide, $\text{Sn}_2(\text{C}_2\text{H}_5)_6$, analogous in constitution to ethane, C_2H_6 . Stannic ethide is a saturated compound, but the other two are unsaturated bodies, capable of uniting with chlorine, bromine, oxygen, and acid radicals, and being thereby converted into compounds of the stannic type.

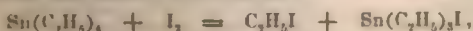
STANNOUS ETHIDE, $\text{Sn}(\text{C}_2\text{H}_5)_2$.—When ethyl iodide and tin-foil are heated together in a sealed glass tube to about 150° or 180° C. (302 – 356° F.), stannic iodethide, $\text{Sn}(\text{C}_2\text{H}_5)_2\text{I}_2$, is produced, crystallizing in colorless needles. The same compound is obtained when tin and ethyl iodide are exposed to the rays of the sun concentrated by a concave mirror. The reaction is considerably facilitated if the tin be alloyed with one-tenth of its weight of sodium. This iodide is decomposed by sodium or zinc, which abstracts the iodine, and leaves stannous ethide in the form of a thick, oily liquid, insoluble in water, having the sp. gr. 1.558, and decomposed by distillation. Stannous ethide combines directly with 2 atoms of chlorine, iodine, and bromine, forming stannic chloroethide, $\text{Sn}^{\text{IV}}(\text{C}_2\text{H}_5)_2\text{Cl}_2$, etc. Exposed to the air, it absorbs oxygen, and is converted into stannic oxoethide, $\text{Sn}^{\text{IV}}(\text{C}_2\text{H}_5)_2\text{O}$, a whitish, tasteless, inodorous powder, which when treated with oxygen acids, yields well-crystallized stannic salts, such as $\text{Sn}(\text{C}_2\text{H}_5)_2(\text{NO}_3)_2$, $\text{Sn}(\text{C}_2\text{H}_5)_2\text{SO}_4$, etc.

STANNOUSO-STANNIC ETHIDE, $\text{Sn}_2(\text{C}_2\text{H}_5)_6$. is always produced in small quantity when stannous ethide is prepared by the methods above mentioned. It is readily obtained in the free state by digesting an alloy of 1 part of sodium and 5 parts of tin with ethyl iodide, exhausting the mass with ether, evaporating the ethereal solution, and exhausting the residue with alcohol. The stannouso-stannic ethide, being insoluble in that liquid, then remains behind. It is a yellow oil, boiling at 180° C. (356° F.), combining directly with chlorine, bromine, and iodine to form two molecules of a stannic compound; e. g.:



also with oxygen, forming distannic oxy-hexethide, $\text{Sn}_2^{\text{IV}}(\text{C}_2\text{H}_5)_6\text{O}$. This oxide is, however, best obtained by distilling stannic oxy-diethide, $\text{Sn}^{\text{IV}}(\text{C}_2\text{H}_5)_2\text{O}$ (above described), with potash. It is an oily liquid, soluble in alcohol, ether, and water; the aqueous solution has a strong alkaline reaction. It is easily acted upon by oxygen-acids, yielding the corresponding sulphate, $\text{Sn}_2(\text{C}_2\text{H}_5)_6\text{SO}_4$, etc.

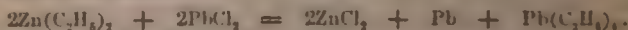
STANNIC ETHIDE, $\text{Sn}^{\text{IV}}(\text{C}_2\text{H}_5)_4$, is produced by the action of zinc ethide on stannic chloride; also by the distillation of stannous ethide: $2\text{Sn}(\text{C}_2\text{H}_5)_2 = \text{Sn} + \text{Sn}(\text{C}_2\text{H}_5)_4$. It is a colorless, nearly odorless liquid, of sp. gr. 1.19, boiling at 181° C. (257.8° F.), and very inflammable, burning with a highly luminous flame. When treated with chlorine, bromine, etc., or with acids, it forms substitution-products: thus, with iodine, it splits up into ethyl iodide and stannic iodotriethide:



with strong hydrochloric acid, it yields ethane and stannic chlorotriethide, $\text{Sn}(\text{C}_2\text{H}_5)_3\text{Cl}$.

Stannous Methide, $\text{Sn}(\text{CH}_3)_2$, and Stannic Methide, $\text{Sn}(\text{CH}_3)_4$, resemble the corresponding ethyl compounds, and are obtained by similar reactions.

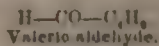
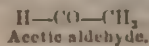
Plumbic Ethide, $\text{Pb}(\text{C}_2\text{H}_5)_4$, is produced by the action of plumbic chloride on zinc ethide:



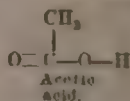
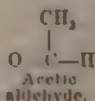
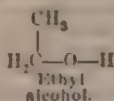
It is a colorless limpid liquid, soluble in ether but not in water. When protected from the air, it boils, with partial decomposition, at about 200°C . (392°F). It is not acted upon by oxygen at ordinary temperatures, but chlorine, bromine, and iodine act violently upon it in the same manner as on stannic ethide, forming plumbic chloro-triethide, $\text{Pb}(\text{C}_2\text{H}_5)_3\text{Cl}$, &c. Plumbic ethide is interesting, as affording a proof that lead is really a tetrad (p. 274).

ALDEHYDES.

THESE are bodies containing the bivalent group CO , associated, on the one hand, with a monatomic alcohol radicle, and on the other with hydrogen; e. g.,



They are derived from primary alcohols by elimination of one or more molecules of hydrogen (H_2), without introduction of an equivalent quantity of oxygen, so that they hold a position intermediate between the alcohols and the acids; thus:



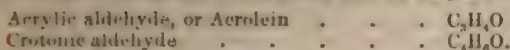
The hydrogen eliminated in the conversion of a primary alcohol into an aldehyde is that which belongs to the group CH_2OH ; consequently a monatomic alcohol can yield but one aldehyde; but a diatomic alcohol can yield two, by removal of H_2 and of 2H_2 ; a triatomic alcohol three, and so on. At present, however, we are acquainted only with aldehydes derived from monatomic and diatomic alcohols.

Aldehydes derived from Monatomic Alcohols.

Of these aldehydes there are two series belonging to the fatty group, viz. :—

1. Aldehydes, $\text{C}_n\text{H}_{2n}\text{O}$, corresponding with the Fatty acids.

| | | | |
|--------------------|---|---------------------|--|
| Formic aldehyde | . . . CH_2O | Caproic aldehyde | . . . $\text{C}_6\text{H}_{12}\text{O}$ |
| Acetic aldehyde | . . . $\text{C}_2\text{H}_4\text{O}$ | Heptanthic aldehyde | . . . $\text{C}_7\text{H}_{14}\text{O}$ |
| Propionic aldehyde | . . . $\text{C}_3\text{H}_6\text{O}$ | Caprylic aldehyde | . . . $\text{C}_8\text{H}_{16}\text{O}$ |
| Butyric aldehyde | . . . $\text{C}_4\text{H}_8\text{O}$ | Eucalic aldehyde | . . . $\text{C}_{10}\text{H}_{20}\text{O}$ |
| Valeric aldehyde | . . . $\text{C}_5\text{H}_{10}\text{O}$ | | |

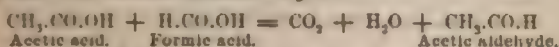
2. Aldehydes, $C_nH_{2n-2}O$, corresponding with the Acrylic acids.

All these aldehydes contain two atoms of hydrogen less than the corresponding alcohols, and one atom of oxygen less than the corresponding acids.

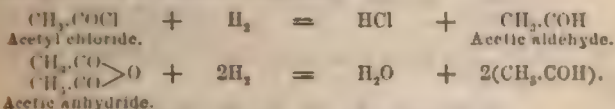
The aldehydes of the fatty groups are produced: 1. By oxidation of primary alcohols, either by the action of atmospheric oxygen, or by that of a mixture of dilute sulphuric acid and potassium dichromate or manganese dioxide, or by the action of chlorine on the alcohol diluted with water, the chlorine in this case decomposing the water, and thus acting as an oxidizing agent; *e. g.* :—



2. By distilling an intimate mixture of the calcium salt of the corresponding acid with calcium formate; *e. g.* :—



3. By the action of nascent hydrogen on the anhydrides and chlorides (chloranhydrides) of the fatty acids :—



4. From the corresponding di-halogen derivatives of the hydrocarbons, by heating with water, or better, with lead oxide :—

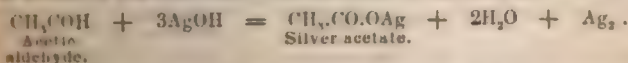


5. By the slow oxidation of albuminous substances by means of manganese dioxide and sulphuric acid.

Some of the aldehydes occur in the essential oils of plants.

The aldehydes are colorless, neutral, volatile liquids, having more or less pungent odors. Only the lower aldehydes are soluble in water.

Reactions.—1. Aldehydes are easily converted by oxidation into the corresponding acids, either on exposure to the air or by contact with moist silver oxide, in the latter case with reduction of metallic silver :—

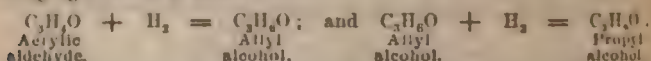


This oxidation takes place with peculiar facility with ammoniacal silver solution, the silver being frequently deposited in a bright specular film.

2. Aldehydes fused with *potash* are converted into the corresponding acids, with evolution of hydrogen; *e. g.*,

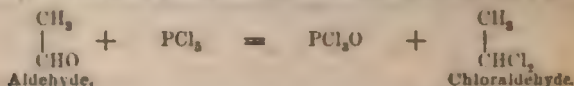


3. *Nascent hydrogen*, evolved by the action of water on sodium amalgam, converts them into the corresponding alcohols; e. g., $C_2H_3O + H = C_2H_5O$. If, however, the aldehyde belongs to a non-saturated series, the action goes further, an additional quantity of hydrogen being then taken up, whereby the alcohol first formed is converted into a saturated alcohol belonging to another series; thus:—



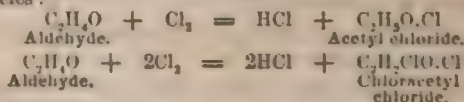
Nascent hydrogen evolved by the action of zinc on sulphuric acid does not appear to unite with aldehydes.

4. *Phosphorus pentachloride* converts aldehydes into chloraldehydes, compounds derived from aldehydes by substitution of Cl_2 for O ; thus:—

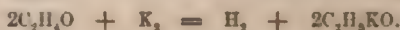


The compounds thus produced are isomeric with the chlorides of the olefines; e. g., acetic chloraldehyde, $CH_3.CHCl_2$, or ethidene chloride, with ethene chloride, $C_2H_2Cl_2$ (p. 517).

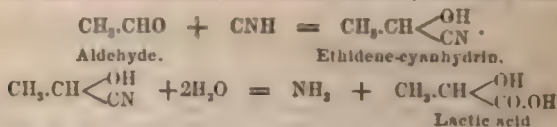
5. *Chlorine and bromine* convert aldehydes into chlorides and bromides of acid radicles:



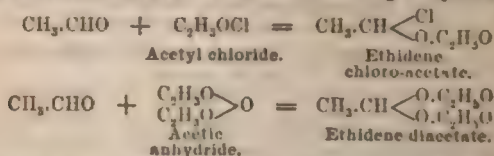
6. The *alkali-metals* dissolve in aldehydes, eliminating an equivalent quantity of hydrogen:



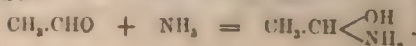
7. Aldehydes heated with *hydrocyanic* and *hydrochloric acid* are converted, first into cyanhydrins, which then, by the action of the hydrochloric acid, or by that of alkalis, are converted into oxy-acids; thus:



8. Aldehyde likewise unites with other carbon-compounds, as with the anhydrides and chlorides of the fatty acids, forming compound ethers:

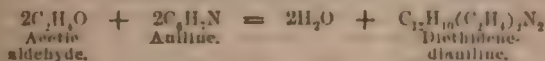


9. Aldehydes combine with ammonia, forming compounds called aldehyde-ammonias, the mode of formation of which is shown in the following equation:—

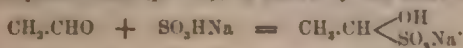


These compounds are easily soluble in water, but insoluble in ether, and are therefore precipitated by ammonia from the ethereal solutions of the aldehydes. They are rather unstable, and are easily resolved by acids into ammonia and the aldehydes.

10. Aldehydes also unite with *aniline*, water being eliminated, and form bases derived from a double molecule of aniline, $(C_6H_7N)_2$, by substitution of two equivalents of a diatomic radicle for four atoms of hydrogen; e. g.,

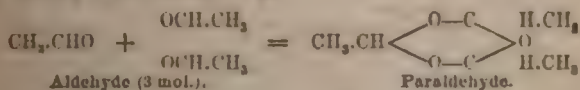


11. All aldehydes unite directly with the *acid sulphites of the alkali-metals*, forming crystalline compounds, which may be regarded as salts of ethidene-oxy-sulphonic acid (p. 606), as shown by the following equation:



From these salts, the aldehydes may be separated by distillation with dilute sulphuric acid or solution of sodium carbonate. The reaction affords a ready means of purifying the aldehydes, and of detecting their presence in mixtures.

12. Under the influence of certain reagents (small quantities of acids, alkalies, and salts) two or more molecules of an aldehyde may unite together, forming a polymeride; e. g.,



ALDEHYDES BELONGING TO THE SERIES $C_nH_{2n}O$.

Formic Aldehyde, CH_2O or $H.CHO$, also called *Methylic aldehyde*.—This compound, discovered by Hofmann, is produced when a current of air charged with vapor of methyl alcohol is directed upon an incandescent spiral of platinum wire; and by suitable condensing arrangements, a liquid may be obtained consisting of a solution of the aldehyde in methyl alcohol. This liquid, rendered slightly alkaline by ammonia, and gently warmed with silver nitrate, yields a beautiful specular deposit of silver, with greater ease even than ordinary acetic aldehyde. The same solution, treated with a few drops of caustic potash, deposits drops of a brownish oil, having the odor of the resin of acetic aldehyde.

Formic aldehyde is likewise obtained by the dry distillation of calcium formate: $Ca(CHO)_2 = CH_2O + CaCO_3$. It has not yet been obtained in the pure state; but on heating the distillate obtained as above, part of the formic aldehyde escapes, and another portion remains as a solid polymeric modification, viz.,

Paraformaldehyde or *Trioxymethene*, $C_3H_4O_3$ or $(CH_2O)_3$, a compound likewise formed by the action of oxide or oxalate of silver on methene iodide, CH_2I_2 , or best by distilling glycollic acid with a small quantity of sulphuric acid. It is a crystalline mass, insoluble in water, alcohol, and ether, melting at $152^\circ C.$ ($305.6^\circ F.$), subliming below $100^\circ C.$ Its vapor density, 1.06, corresponds with the formula CH_2O , showing that the molecule $C_3H_4O_3$ is split up when heated into three molecules of formaldehyde. On cooling, however, the triple molecule is reproduced. $C_3H_4O_3$ is also converted into CH_2O when heated with water to $130^\circ C.$ ($266^\circ F.$).

When ammonia is passed over paraformaldehyde, hexamethenamine, $C_6H_{12}N_4 = (CH_2)_6N_4$, is produced, a base which crystallizes from alcohol in shining rhombohedrons, and sublimes without alteration when cautiously heated. It is a monacid base, forming crystalline salts, the hydrochloride, $C_6H_{12}N_4 \cdot HCl$, for example. By boiling with dilute acids it is reconverted into formaldehyde.

Parathioformaldehyde or *Trithiomethene*, $(CH_2)_3S_3$, is produced by passing hydrogen sulphide into the aqueous solution of formaldehyde, also by the action of zinc and hydrochloric acid on carbon bisulphide, and by heating methene iodide with potassium sulphide in alcoholic solution. It is a solid body having an alliaceous odor, is insoluble in water, but dissolves in alcohol, and crystallizes therefrom in slender needles, melting at 218° , and easily subliming. The vapor-density agrees with the formula $C_3H_6S_3$, whence it is inferred that solid paraformaldehyde is correctly represented by the formula $C_3H_2O_3$. The thionaldehyde, $C_3H_6S_2$, heated to $170^\circ C.$ ($338^\circ F.$) with silver sulphate, is converted into $C_3H_6O_3$.

Acetic Aldehyde, or **Acetaldehyde**, $C_2H_4O = CH_3 \cdot CHO = C_2H_3O \cdot H$, also called *Ethyl Aldehyde*, but more generally by the simple name *aldehyde*.*—This substance is formed by oxidation of ethyl-alcohol; also among other products, when the vapor of ether or alcohol is transmitted through a red-hot tube; by the action of chlorine on weak alcohol; and by the other general reactions above mentioned. It is best prepared by the following process: 6 parts of oil of vitriol are mixed with 4 parts of rectified spirit of wine, and 4 parts of water; this mixture is poured upon 6 parts of powdered manganese dioxide contained in a capacious retort, in connection with a condenser cooled by ice-cold water; gentle heat is applied, and the process is interrupted when 6 parts of liquid have passed over. The distilled product is put into a small retort, with its own weight of calcium chloride, and redistilled; and this operation is repeated. The aldehyde, still retaining alcohol and other impurities, is mixed with twice its volume of ether, and saturated with dry ammoniacal gas; a crystalline compound of aldehyde and ammonia then separates, which may be washed with a little ether, and dried in the air. From this substance the aldehyde may be separated by distillation in a water-bath with sulphuric acid diluted with an equal quantity of water; by careful rectification from calcium chloride, at a temperature not exceeding $30.5^\circ C.$ ($86.9^\circ F.$), it is obtained pure and anhydrous.

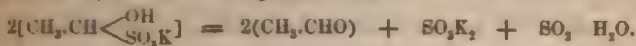
Considerable quantities of aldehyde occur in the "first runnings" obtained in the manufacture of alcohol from sugar-beet and from potatoes, being probably formed by oxidation of the spirit during the filtration through charcoal, to which it is subjected for the removal of fusel-oil and other impurities.

Aldehyde is a limpid, colorless liquid, of characteristic ethereal odor, which when strong, is exceedingly suffocating. It has a density of 0.807 at 60° , boils at $21-22^\circ C.$ ($69.8^\circ-71.6^\circ F.$), and mixes in all proportions with water, alcohol, and ether: it is neutral to test-paper, but becomes acid on exposure to air, from production of acetic acid: under the influence of platinum-black this change is very speedy. When a solution of aldehyde is heated with caustic potash, a brown resin-like substance is produced, the so-called *aldehyde-resin*. It reduces silver oxide at a gentle heat, without evolution of gas, the metal being deposited on the inner surface of the vessel as a brilliant and uniform film; the liquid contains silver acetate.

* Alcohol dehydrogenatum.

The principal reactions of aldehyde have been already mentioned (p. 666). It is converted by nascent hydrogen into ethyl alcohol, by oxidation into acetic acid: by phosphorus pentachloride into chloraldehyde or ethidene dichloride, $\text{CH}_2=\text{CHCl}_2$. It unites with the acid sulphites of the alkali-metals, forming compounds like the ammonium salt,

$\text{CH}_3\text{CH} \begin{smallmatrix} \text{OH} \\ \text{O.SO}_2(\text{NH}_4) \end{smallmatrix}$, which are resolved at 100° into aldehyde, sulphurous oxide, and neutral sulphites; thus:



Aldehyde unites also with *acetic oxide*, forming the compound $\text{C}_4\text{H}_6\text{O}$. $(\text{CH}_3\text{CO})_2\text{O}$ or $\text{CH}_3\text{CH} \begin{smallmatrix} \text{OC}_2\text{H}_5\text{O} \\ \text{OC}_2\text{H}_5\text{O} \end{smallmatrix}$, and with *ethyl oxide*, forming ethidene diethylate or acetal, $\text{CH}_3\text{CH} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$; in like manner with *methyl acide*, forming ethidene dimethylate, $\text{CH}_3\text{CH}(\text{OCH}_3)_2$ (p. 606).

With dry *hydrogen cyanide*, aldehyde forms the compound $\text{CH}_3\text{CH} \begin{smallmatrix} \text{OH} \\ \text{CN} \end{smallmatrix}$, a liquid soluble in water and in alcohol, boiling at 183°C . (361.4°F .), with partial decomposition into aldehyde and hydrogen cyanide, and converted, by heating with strong hydrochloric acid or with alkalies, into α -lactic acid, $\text{CH}_3\text{CH} \begin{smallmatrix} \text{OH} \\ \text{CO}_2\text{H} \end{smallmatrix}$.

Aldehyde-ammonia, $\text{C}_2\text{H}_4\text{O.NH}_3 = \text{CH}_3\text{CH} \begin{smallmatrix} \text{OH} \\ \text{NH}_2 \end{smallmatrix}$, obtained by passing dry ammonia gas into an ethereal solution of aldehyde, crystallizes in large shining rhombohedrons; it has a mixed odor of ammonia and turpentine, dissolves very easily in water, with less facility in alcohol, and with difficulty in ether; melts at about 76°C . (168.8°F .), and distills unchanged at 100° . Acids decompose it, with production of ammoniacal salts and separation of aldehyde. Hydrogen sulphide converts it into thialdine, $\text{C}_6\text{H}_{12}\text{NS}_2$. Sulphurous oxide gas is rapidly absorbed by a solution of aldehyde-ammonia, forming the crystalline compound $\text{C}_2\text{H}_4\text{ONH}_2.\text{SO}_2$, isomeric with taurine (p. 605), and with the compound formed by direct combination of aldehyde with acid ammonium sulphite.

POLYMERIC MODIFICATIONS OF ALDEHYDE.—Pure anhydrous aldehyde, treated at ordinary temperatures with a small quantity of gaseous hydrochloric acid, sulphurous oxide, or carbonyl chloride (phosgene), or of zinc chloride or strong sulphuric acid, is converted into a polymeride, called *paraldehyde*, which crystallizes on cooling the liquid to 0° in large transparent prisms, melting at 10.5°C . (50.9°F .) to a liquid which boils at 124°C . (255.2°F .), has a specific gravity of 0.998 at 15°C . (59°F .), and a vapor-density three times as great as that of aldehyde itself: hence its molecular formula is $\text{C}_6\text{H}_{12}\text{O}_3$. When distilled in contact with either of the reagents above mentioned, it is reconverted into ordinary aldehyde, but it does not undergo this change when heated alone.

When either of the same reagents acts on aldehyde cooled by a freezing mixture, another polymeric modification is formed, called *metalddehyde*, which also crystallizes in transparent prisms or in white needles, but differs from paraldehyde in subliming when heated without previous fusion, and in being at the same time partly reconverted into aldehyde. In consequence of this transformation, its vapor-density, and therefore its molecular formula, have not been determined.

When aldehyde is left for some time in contact with dilute hydrochloric

Halogen Derivatives of Aldehyde.

Monochloraldehyde, $\text{CH}_2\text{Cl}.\text{CHO}$, formed by the action of acid on chloroacetal, $\text{CH}_2(\text{Cl}-\text{CH}(\text{OC}_2\text{H}_5)_2)$, is known only in solution. By exposure to the air, and by the action of silver or silver oxide, it is converted into chloroacetic acid.

Dichloraldehyde, $\text{CHCl}_2.\text{CHO}$, produced by distillation of chloroacetal with strong sulphuric acid, is a liquid insoluble in water, boiling at 88°C . (190.4°F). By keeping, it is gradually converted into two solid polymeric modifications, one of which is amorphous and reconverted into liquid dichloraldehyde at 120°C . (248°F); the other crystallizes from alcohol in large prisms, melts at 130°C and does not pass into the liquid modification till heated to 464°F .

Trichloraldehyde, or **Chloral**, $\text{CCl}_3.\text{CHO}$, is formed by the action of chlorine on ethyl alcohol. To prepare it, chlorine is added to absolute alcohol as long as hydrochloric acid continues to be formed; the product is agitated with three times its volume of strong sulphuric acid. On gently warming the mixture in a water-bath, the acid separates as an oily liquid, which floats on the surface of the alcohol; it is purified by distillation from fresh oil of vitriol, and after addition of a small quantity of quicklime, which must be kept complete until the liquid until the end of the operation. Chloral has also been prepared from starch, by distillation with hydrochloric acid and manganese dioxide.

Chloral is a thin, oily, colorless liquid, of peculiar, pungent odor: it has but little taste. When dropped upon paper it leaves a brown stain, which is not, however, permanent. It has a density of 1.48 at 94°C . (201.2°F), and changes on prolonged keeping into trichloroacetic acid. Chloral is freely soluble in water, alcohol, and ether, and its solution is not affected by alkaline solutions. Specific gravity 1.48 at 94°C .

ing taste, and produces sleep when taken internally or introduced under the skin. Strong sulphuric acid decomposes it into water and alcohol.

With *hydrogen sulphide*, chloral forms, in like manner, a crystalline sulphhydrate, $\text{CCl}_3\text{CH} \begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$, which melts at 77°C . (170.6°F .), and boils at 123°C . (251.6°F .).

With *alcohol*, chloral forms an alcoholate, $\text{CCl}_3\text{CH} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OH} \end{smallmatrix}$, which is a crystalline body, melting at 56°C . (132.8°F .), and boiling at $114^\circ\text{--}115^\circ \text{C}$. ($237.2^\circ\text{--}239^\circ \text{F}$.), and decomposed by strong sulphuric acid, with reproduction of chloral. Treated with *acetyl chloride*, it is converted into the acetic ether, $\text{CCl}_3\text{CH} \begin{smallmatrix} \text{O.C}_2\text{H}_5 \\ \text{O.C}_2\text{H}_5\text{O} \end{smallmatrix}$, which boils at 198°C . (388.4°F .).

Dibromaldehyde, CHBr_2CHO , formed by direct bromination of aldehyde, is a liquid which boils at $140^\circ\text{--}142^\circ \text{C}$. ($284^\circ\text{--}287.6^\circ \text{F}$.), is converted on standing into a solid polymeride, forms a crystalline hydrate, and unites with hydrogen cyanide, forming the compound, $\text{CHBr}_2\text{CH} \begin{smallmatrix} \text{CN} \\ \text{OH} \end{smallmatrix}$, convertible into dibromolactic acid.

Tribromaldehyde or **Bromal**, CBr_3CHO , formed by the action of bromine on alcohol, is a liquid very much like chloral, boiling at $172^\circ\text{--}177^\circ \text{C}$. ($341.6^\circ\text{--}343.4^\circ \text{F}$.), and decomposed by alkalis into formic acid and bromoform. It forms a solid hydrate, melting at 53°C . (127.4°F .), an alcoholate which melts at 44°C . (111.2°F .), and decomposes at 100° , and with hydrogen cyanide the compound, $\text{CBr}_3\text{CH} \begin{smallmatrix} \text{CN} \\ \text{OH} \end{smallmatrix}$, convertible into tribromolactic acid.

Sulphur-derivatives of Aldehyde.—When hydrogen sulphide is passed through aqueous aldehyde, a compound of aldehyde and thioaldehyde is produced, in the form of an oil, having an offensive odor, solidifying at -8°C . (17.6°F .), and converted by contact with hydrochloric acid into parathioaldehyde, $(\text{C}_2\text{H}_5\text{S})_2$. This compound, analogous to paraldehyde, forms white needles, insoluble in water, and subliming at 47°C . (113°F .). Its vapor density agrees with the formula, $\text{C}_6\text{H}_{12}\text{S}_6$.

On passing hydrogen sulphide into an aqueous solution of aldehyde-ammonia, thialdine, $\text{C}_6\text{H}_{12}\text{NS}_2$, separates in large colorless crystals, melting at 43°C . (109.4°F .), slightly soluble in water, easily in alcohol and ether, and having an offensive odor. It is a strong base; its hydrochloride has the composition $\text{C}_6\text{H}_{12}\text{NS}_2\text{HCl}$.

On mixing an alcoholic solution of aldehyde-ammonia with carbon bisulphide, carbothialdine, $\text{C}_6\text{H}_{10}\text{N}_2\text{S}_3$, is formed in large shining crystals, separable by boiling with acids into aldehyde, carbon bisulphide, and ammonia.

Propionic Aldehyde, $\text{C}_3\text{H}_6\text{O} = \text{CH}_3\text{CH}_2\text{CHO}$, prepared by oxidation of normal propyl alcohol, or by distilling a mixture of calcium propionate and formate, is very much like acetaldehyde, has a specific gravity of 0.804 at 20°C . (68°F .), boils at 49°C . (120.2°F .), and dissolves in 5 volumes of water. With phosphorus pentachloride it forms propidene chloride, $\text{CH}_3\text{CH}=\text{CHCl}_2$.

The higher aldehydes of the series are susceptible of isomeric modifications analogous to those of the primary alcohols. Only a few of these are,

however, known: thus, of the four possible 5-carbon aldehydes, and to the four primary pentyl alcohols, two only have yet been obtained.

The following table exhibits the specific gravities and boiling points of these higher aldehydes. All of them are liquid at ordinary temperatures except palmitic aldehyde, formed by oxidation of cetyl alcohol, which is a white crystalline mass:—

| Aldehydes. | Boiling Point. | Specific gravity. |
|---|--|-----------------------------|
| Butyric { Normal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
Iso, $(\text{CH}_3)_2\text{CHCHO}$ | 77° C. (167° F.)
61° C. (141.5° F.) | 0.834 at 0°
0.822 at 10° |
| Valeric { Normal, $\text{CH}_3(\text{CH}_2)_3\text{CHO}$
Iso, $(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$ | 102° C. (215.6° F.)
92-93° C. (197.6-199.4° F.) | 0.768 at 12° C.
(F.) |
| Caproic (Iso), $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{CHO}$ | 121° C. (249.5° F.) | |
| Enanthyllic, $\text{CH}_3(\text{CH}_2)_5\text{CHO}$ | 154° C. (309.2° F.) | 0.827 |
| Palmitic, $\text{C}_{16}\text{H}_{32}\text{O}$. | melts at 56° C. (133° F.) | |

Isobutyric aldehyde treated with a small quantity of strong sulphuric acid is converted into paralobutyric aldehyde, $(\text{C}_4\text{H}_8\text{O})_3$, which crystallizes in shining needles, melting at 60° C. (140.2° F.), and boiling at 194° C. (381.2° F.).

Normal butyric aldehyde, heated with alcoholic ammonia to a temperature not exceeding 100°, yields two bases, dibutyraldine, $\text{C}_8\text{H}_{16}\text{NO}$, and tetra butyraldine, $\text{C}_{16}\text{H}_{32}\text{NO}$, the former of which, when subjected to dry distillation, gives off H_2O , and is converted into paraconine, $\text{C}_{16}\text{H}_{32}\text{N}$, an oily base, very much like the conine of hemlock.

Trichlorobutyric aldehyde or *Butyric chloral*, $\text{C}_4\text{H}_3\text{Cl}_3\text{O}$ (formerly supposed to be crotonic chloral, $\text{C}_4\text{H}_3\text{Cl}_3\text{O}$), is formed, together with several products, by the action of chlorine on acetaldehyde. It is a liquid boiling at 155°-165° C. (311°-329° F.).

Isovaleric aldehyde or *Valeral*, heated with alcoholic ammonia, yields two bases, valeridine, $\text{C}_{10}\text{H}_{18}\text{N}$, and valeritrine, $\text{C}_{15}\text{H}_{27}\text{N}$, the latter of which is a liquid, boiling at 250°-260° C. (482°-500° F.), and similar to conine.

Enanthyllic Aldehyde or *Enanthol*, is formed in the dry distillation of castor-oil. It oxidizes in the air to enanthylic acid, and is converted into nascent hydrogen into normal heptyl alcohol.

ALDEHYDES OF THE SERIES, $\text{C}_n\text{H}_{2n-2}\text{O}$.

These aldehydes are related to the alcohols of the allylic series in the same manner as the aldehydes, $\text{C}_n\text{H}_{2n}\text{O}$, are related to the fatty alcohols. They are unsaturated compounds, and capable of taking up 2 atoms of monatomic element or radicle.

Acrylic Aldehyde or **Acrolein**, $\text{C}_3\text{H}_4\text{O}=\text{CH}_2=\text{CH}-$ the lowest member of the series, is produced:

1. By the oxidation of allyl alcohol.

2. By the dehydration of glycerin, when that substance is heated with phosphoric oxide, strong sulphuric acid, or acid potassium sulphate, $\text{C}_3\text{H}_8\text{O}_3-2\text{H}_2\text{O}=\text{C}_3\text{H}_4\text{O}$.

It is always produced in the destructive distillation of neutral fats containing glycerin, and is the cause of the intolerably pungent odor attending that process.

Pure acrolein is a thin, colorless, highly volatile liquid, lighter than water, and boiling at 52.2°C . (126°F .). Its vapor is intensely irritating. It is sparingly soluble in water, freely in alcohol and ether.

Acrolein, by keeping, undergoes partial decomposition, yielding a white, flocculent, indifferent body, diacetyl; the same substance is sometimes produced, together with acrylic acid, by exposure to the air. In contact with alkalis, acrolein suffers violent decomposition, producing, like aldehyde, a resinous body. When exposed for some time to the air, or mixed with silver oxide, it is rapidly oxidized into acrylic acid, $\text{C}_3\text{H}_4\text{O}_2$.

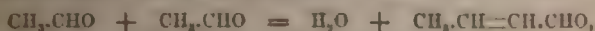
Nascent hydrogen converts it into allyl alcohol. With phosphorus pentachloride it yields the compound $\text{CH}_2=\text{CH}-\text{CHCl}_2$, a liquid boiling at 84°C . (183.2°F .). With hydrochloric acid acrolein forms a crystalline compound, $\text{C}_3\text{H}_4\text{O}.\text{HCl}$, which melts at 32°C . (89.6°F .), and is resolved by distillation into hydrochloric acid and acrolein.

Acrolein mixed with alcoholic ammonia is immediately converted into acrolein-ammonia, $\text{C}_3\text{H}_3\text{NO}$:



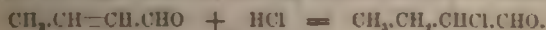
This compound is a yellowish mass, which turns brown on drying. It forms amorphous salts, and yields picoline, $\text{C}_6\text{H}_7\text{N}$, by distillation.

Crotonic Aldehyde, $\text{C}_4\text{H}_6\text{O} = \text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$, is prepared by heating acetaldehyde to 100° with dilute hydrochloric acid, or with zinc chloride, and a little water:



alcohol being probably formed as an intermediate product.

Crotonic aldehyde is a colorless liquid, having an extremely pungent odor, and boiling at $104^{\circ}-105^{\circ}\text{C}$. ($219.2^{\circ}-221^{\circ}\text{F}$.). In contact with the air, or with moist silver oxide, it is easily oxidized to crotonic acid. It unites with hydrogen chloride, forming monochlorobutyric aldehyde:

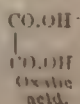
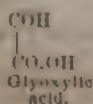


Aldehydes derived from Diatomic Alcohols.

Diatomic alcohols can yield by oxidation two classes of aldehydes, according as one or two molecules of hydrogen (H_2) are removed. Propene glycol, $\text{C}_3\text{H}_8\text{O}_2$, for example, might yield the two aldehydes, $\text{C}_3\text{H}_6\text{O}_2$, and $\text{C}_3\text{H}_4\text{O}_2$. Only a few of these compounds have, however, been obtained.

Of aldehydes derived from the glycols, $\text{C}_n\text{H}_{2n+2}\text{O}_2$, only three are at present known, viz., glyoxal, $\text{C}_2\text{H}_2\text{O}_2$, which is the second aldehyde of ordinary glycol, $\text{C}_2\text{H}_6\text{O}_2$; aldol, $\text{C}_3\text{H}_4\text{O}_2$, which is the first, and succinic aldehyde, $\text{C}_4\text{H}_4\text{O}_2$, which is the second aldehyde of butene glycol.

Glyoxal, $\text{C}_2\text{H}_2\text{O}_2$, and the aldehydic acid, glyoxylic acid, $\text{C}_2\text{H}_2\text{O}_3$, are intermediate in composition between glycol and oxalic acid:



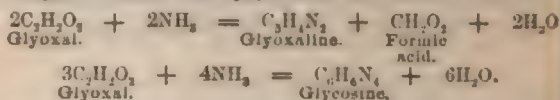
Both are formed as intermediate products in the oxidation of glycols, and are converted by further oxidation into oxalic acid. They are, however, most easily obtained by oxidizing ethyl alcohol with nitric acid.

Alcohol (2 parts) is introduced into a tall glass cylinder, 1 part of nitric acid is poured into the vessel through a funnel, the tube of which reaches to the bottom, and afterwards 1 part of fuming nitric acid is introduced in the same way, so as to form three distinct layers of liquid. The mixture is left to itself at a temperature of 20°C – 23°C . (68°F – 71.6°F .) until the liquids have become mixed; after which the mixture is evaporated in a water-bath, diluted with water, saturated with chalk at the boiling point, then filtered, and the filtrate is mixed with alcohol, whereupon glyoxal and glyoxylate of calcium are precipitated, and glyoxal remains in solution. On recrystallizing the calcium salts, the glyoxylate crystallizes out, and afterwards the glycollate. The glyoxal is separated from the glycollate by agitation with acid sodium sulphite, with which it forms a crys- tal compound; this sodium compound treated with barium chloride yields the corresponding barium compound; and from this the glyoxal may be separated by dilute sulphuric acid.

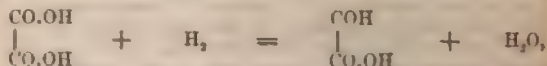


on evaporating the solution obtained in the manner just described, it forms a transparent, amorphous, deliquescent mass, very soluble in water, alcohol, and ether. It reduces an ammoniacal solution of silver nitrate, forming a silver speculum. Nitric acid oxidizes it to glycollic and oxalic acids, forming a double aldehyde (containing the group COH twice) it unites with two molecules of acid potassium sulphite, forming the compound $(\text{SO}_3\text{KH})_2$. When its solution in acetic acid is left in contact with a quantity of hydrochloric acid, a condensation-product is formed, $\text{C}_{12}\text{H}_{12}\text{O}_{12}$.

Fixed caustic alkalies and alkaline earths convert glyoxal into glycollic acid, *e. g.*, $\text{C}_2\text{H}_2\text{O}_2 + \text{KOH} = \text{C}_2\text{H}_3\text{KO}_2$. A syrupy solution of glyoxal heated with a strong solution of aqueous ammonia yields two line bases, glyoxaline and glycosine:



Glyoxylic or Glyoxalic Acid, $\text{C}_2\text{H}_2\text{O}_3 = \text{CHO}-\text{CO}_2\text{H}$, is formed by the oxidation of alcohol as above described; also by reducing oxalic acid with zinc and hydrochloric acid:



and by heating dichloroacetic acid with silver oxide, or ethylic dichloroacetate with water to 120°C . (248°F .):

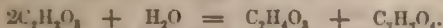


When concentrated, it forms a thick syrup easily soluble in water, and distils undecomposed with aqueous vapor.

The glyoxylates contain 1 molecule of water very closely combined, excepting the ammonium salt, which is anhydrous.

alt, $C_4H_7O_2.NH_4$, crystallizes in needles, and dissolves easily in water. The silver salt, $C_4H_7O_2Ag + H_2O$, is a white crystalline precipitate; the calcium salt, $(C_4H_7O_2)_2Ca + 2H_2O$, forms hard prisms, sparingly soluble in water.

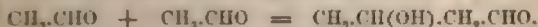
Glycolic acid is readily oxidized to oxalic acid. By boiling its calcium salt in water, it is resolved into glycollic and oxalic acids:



When hydrogen (zinc and hydrochloric acid), it is converted into glycolic acid.

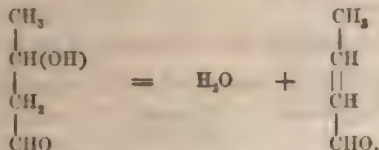
Glycolic acid is both acid and aldehyde. Its aldehydic nature is shown by its power of reducing an ammoniacal silver solution, and of forming salts with alkaline bisulphites.

$C_4H_7O_2$, the aldehyde of butene glycol, is polymeric with acetaldehyde, and is formed by combination of two molecules of that body, under the influence of dilute hydrochloric acid; thus:

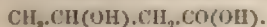


A mixture of acetaldehyde and dilute hydrochloric acid is left for two days; it acquires a yellow color. The liquid is then neutralized with sodium carbonate, and shaken up with ether; the ether is evaporated; the residue which remains is evaporated in a vacuum.

The residue is a colorless inodorous liquid, of specific gravity 1.120 at 0° , not miscible with water. On standing it changes to a viscid liquid, which is poured out of the containing vessel. In a vacuum it distils between $50^\circ C.$ ($122^\circ F.$) and $105^\circ C.$ ($221^\circ F.$), but when heated under pressure it gives off water, and is converted into crotonic aldehyde:



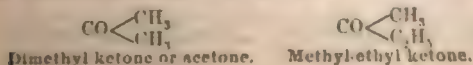
The silver salt is precipitated from the ammonio-nitrate, and when heated with water and silver oxide, is converted into β -oxybutyric acid:



Isobutyric Aldehyde, $C_4H_8O_2$, $\begin{array}{c} CH_3.CO.H \\ | \\ CH_2.CO.H \end{array}$, is a liquid soluble in water, boiling at $201^\circ - 203^\circ C.$ ($393.8^\circ - 397.4^\circ F.$). By oxidation it is converted into normal oxyisobutyric acid and succinic acid.

KETONES.

These bodies contain the group CO associated with two monatomic alcohols, which may either be the same or different, *c. g.*,



The ketones of this group, containing two equivalents of alcohol-radicle, are produced :—

1. By the action of carbon monoxide on sodium ethidealogues :—



For example :—



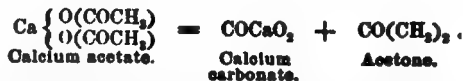
2. By the action of zinc-methyl and its homologues on chlorides, $\text{C}_n\text{H}_{2n-1}\text{OCl}$; e. g. :—



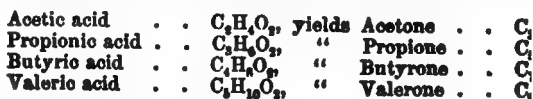
3. By the oxidation of the secondary alcohols ; thus :—



4. By the dry distillation of the calcium-salts of the fatty acids :

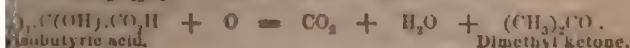


The ketones formed in this manner from the successive members of the fatty acid series differ from one another by twice CH_2 ; thus :



formation of aldehydes by distilling a mixture of a formate with of another fatty acid (p. 665), is a particular case of this last

are also formed: 5. By the gradual oxidation of the acids of a series, $C_nH_{2n}O_2$, with chromic acid mixture:—



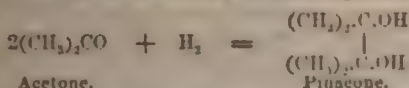
the action of alkalis on the carbo-ketonic acids (*q. v.*).

The dry distillation of wood, sugar, and many other carbon

ketone is isomeric with an aldehyde belonging to the same series; acetone is isomeric with propionic aldehyde, C_3H_5COH ; butyrene, C_4H_7 , with cinnamyllic aldehyde, C_6H_5COH , etc. Formic acetone, identical with formic aldehyde.

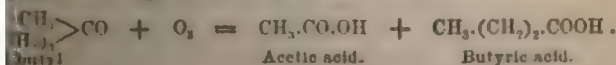
are, for the most part, volatile liquids, insoluble in water, and of reducing an ammoniacal silver solution. Those in which the CO is associated with a methyl group, resemble the aldehydes in crystalline compounds with alkaline bisulphites, from which they may be liberated by distillation with an alkali. Ketones differ from aldehydes: 1. In not being converted by oxidation into the corresponding acids.—2. In being converted by nascent hydrogen into secondaries, whereas the aldehydes are converted into primary alcohols, and not combining with aniline.

formation of secondary alcohols by hydrogenation of ketones is due to a small amount, with a condensation of two ketone molecules, in the formation of a diatomic alcohol (a pinacone); *e. g.*:—

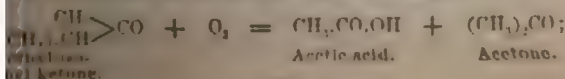


like aldehydes, unite with hydrogen cyanide, forming cyanides. Acetone, for example, yielding $(CH_3)_2C \begin{array}{c} OH \\ \diagup \\ N \end{array}$, which, by the action of acids or alkalis, may be converted into the corresponding oxy-

are not convertible by oxidation into acids containing the same number of carbon-atoms as themselves. When boiled with chromic acid they decompose in such a manner that the group CO separates in combination with the lower alcohol-radicle, and forms an acid; while, the other radicle is a primary radicle, it is likewise oxidized to an acid, *e. g.* iso, according to the constitution of the radicle; thus:—



On the other hand, the higher radicle is secondary, it will be oxidized to an acid, which will be further split up by oxidation:

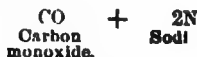


hol-radicle, are produced :—

1. By the action of carbon monoxide :—



For example :—



2. By the action of zinc methide, $\text{C}_2\text{H}_3\text{OCl}$;



3. By the oxid



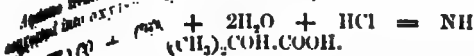
Isopropyl a

4. By the d

The keton
fatty acid

Acet
Pr
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Va

Acetone treated with hydrocyanic acid, water, and hydro



acetone is converted into aceto

monobromopropene



passing the vapor of redness, and by the starch, gum, and w

distillation of acetat
convenient for the purpo
carbonate, and after

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C. (131.9° F.): the dens
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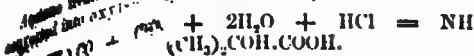
into pseudopropyl alcohol (C
acetone doubles its molecule
by converted into a crystall

and mixture, acetone is convert
water being for the most part fi



Acetic acid. Formic

Acetone treated with hydrocyanic acid, water, and hydro



acetone is converted into aceto

water, boiling at 119°C . (246.2°F .), and emitting a flow of tears.

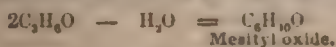
These there are two, viz. :

and $\text{CH}_3\text{Cl.CO.CH}_3\text{Cl}$.
Symmetrical.

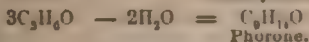
Direct chlorination of acetone, is an oily liquid, boiling at 21°C . (69.8°F .), and boiling at 120°C .

Acetic acid, obtained by oxidation of symmetrical acetone, $\text{HOH.CH}_2\text{Cl}$, crystallizes in rhombic plates, melts at 17°C , and boils at $172^{\circ}\text{--}174^{\circ}\text{C}$. ($341.6^{\circ}\text{--}345.2^{\circ}\text{F}$.).

Products of Acetone.—When acetone is subjected to dehydrating agents, such as sulphuric acid, quick-lime, or hydrochloric acid, two or more molecules of it unite to form a condensation-product; thus :



Mesityl oxide.

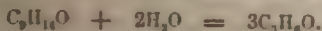


Phorone.

Bodies are best prepared by saturating acetone with gaseous hydrochloride, leaving the liquid to itself for some time, and treating the residue with alcoholic potash. On dilution with water an oily liquid is obtained, consisting of mesityl oxide and phorone, which may be separated by fractional distillation.

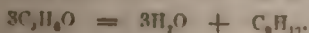
Mesityl Oxide, $\text{H}_3\text{C} > \text{C} = \text{CH.CO.CH}_3$, is a colorless oil, smelling like mint, and boiling at 130°C . (266°F .). Treated with phosphorus chloride, it is converted into the chloride, $\text{C}_6\text{H}_{10}\text{Cl}_2$. By boiling with sulphuric acid, it is resolved into two molecules of acetone. An isomeric compound, called Metacetone, is formed by distilling with lime; it is a liquid boiling at 84°C . (183.2°F .).

Phorone, $\text{C}_9\text{H}_{14}\text{O}$, probably $\text{H}_3\text{C} > \text{C} = \text{CH} - \text{C} \begin{smallmatrix} \nearrow \text{CH} - \text{CO} - \text{CH}_3 \\ \searrow \text{CH}_3 \end{smallmatrix}$.—This crystallizes in large yellowish prisms, melts at 28°C . (82.4°F .), and boils at 196°C . (384.8°F .), and when boiled with dilute sulphuric acid and water, and is resolved into 3 molecules of acetone :



Camphorone, produced by heating acetone with quick lime, and camphrene, obtained from camphoric acid, appear to be isomeric with the phorone obtained as above.

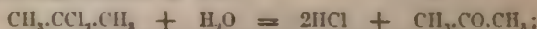
Acetone heated with strong sulphuric acid yields a distillate of mesityl trimethyl benzene, a body belonging to the aromatic group :



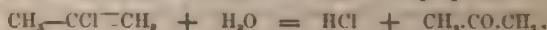
The same body is formed by the action of sulphuric acid on phorone. Ketones heated with sulphuric acid likewise yield derivatives of

and if the higher radiolo is tertiary, such as $C(CH_3)_3$, it will be immediately split up.*

Dimethyl Ketone.—**Acetone**, $CO(CH_3)_2$.—This compound is formed: 1. By the dry distillation of acetates.—2. By oxidation of pseudopropyl alcohol.—3. By the action of water at 180° – 200° C. (356° – 392° F.) on acetone chloride or bromide (p. 519):



or on propene chloride (or bromide), $CH_3.CHCl.CH_2Cl$ (in which case a molecular transposition of H and Cl must be supposed to take place in the first instance), or on monochloro- or monobromopropene:



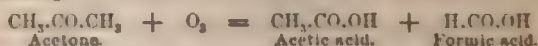
4. Together with other products, by passing the vapor of strong acetic acid through an iron tube heated to dull redness, and by the dry distillation of citric acid, tartaric acid, sugar, starch, gum, and wood: hence it occurs in crude wood-spirit.

Acetone is best prepared by the dry distillation of acetates, the calcium or the lead salt being the most convenient for the purpose. The crude distillate is saturated with potassium carbonate, and afterwards rectified in a water-bath from calcium chloride.

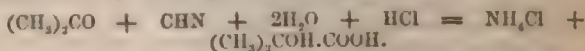
Pure acetone is a colorless limpid liquid, of peculiar odor: it has a density of 0.792, and boils at 55.5° C. (131.9° F.): the density of its vapor (referred to air) is 2.022. Acetone is very inflammable, and burns with a bright flame: it is miscible in all proportions with water, alcohol, and ether.

Nascent hydrogen converts it into pseudopropyl alcohol (p. 579); but at the same time a portion of the acetone doubles its molecule, and likewise takes up hydrogen, being thereby converted into a crystalline substance, pinacone, $C_6H_{14}O_2 = 2C_3H_8O + H_2$.

By oxidation with chromic acid mixture, acetone is converted into acetic and formic acids, the latter being for the most part further oxidized to H_2O and CO_2 .



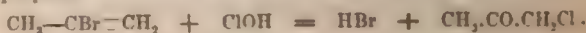
Acetone treated with hydrocyanic acid, water, and hydrochloric acid is converted into oxyisobutyric (acetonie) acid:



By phosphorus pentachloride, acetone is converted into acetone chloride or methylchloroacetol, $CH_3.CCl_2.CH_3$; similarly with PBr_5 . With P_2S_5 , it forms thioacetone, $CH_3.CS_2.CH_3$, a yellowish offensive-smelling liquid, boiling at 183° – 185° C. (361.4° – 365° F.), insoluble in water.

Chlor- and Brom-acetones.—These compounds are formed by the direct action of chlorine and bromine on acetone, and in other ways.

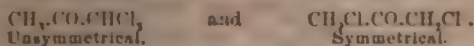
Monochloroacetone, $CH_3.CO.CH_2Cl$, is formed by passing chlorine into cold acetone, and by the action of hypochlorous acid on monochloro- or monobromopropene:



* See Watts's Dictionary of Chemistry, 2d Supplement, 711.

It is a liquid, insoluble in water, boiling at 119°C . (246.2°F .), and emitting vapors which excite a copious flow of tears.

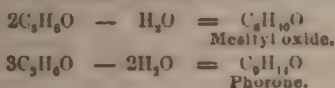
Dichloracetones, $\text{C}_2\text{H}_4\text{Cl}_2\text{O}$.—Of these there are two, viz.:



The former, produced by direct chlorination of acetone, is an oily liquid, having a density of 1.236 at 21°C . (69.8°F .), and boiling at 120°C . (248°F .).

The symmetrical modification, obtained by oxidation of symmetrical dichlorhydrin, $\text{CH}_2\text{Cl.CH(OH).CH}_2\text{Cl}$, crystallizes in rhombic plates, melts at 43°C . (109.4°F .), and boils at $172^{\circ}\text{--}174^{\circ}\text{C}$. ($341.6^{\circ}\text{--}345.2^{\circ}\text{F}$.).

Condensation-products of Acetone.—When acetone is subjected to the action of dehydrating agents, such as sulphuric acid, quick-lime, lime chloride, or hydrochloric acid, two or more molecules of it unite together, with separation of water, to form a condensation-product; thus:

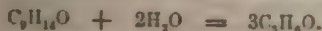


These bodies are best prepared by saturating acetone with gaseous hydrogen chloride, leaving the liquid to itself for some time, and treating the product with alcoholic potash. On dilution with water an oily liquid is obtained, consisting of mesityl oxide and phorone, which may be separated by fractional distillation.

Mesityl Oxide, $\text{C}_4\text{H}_6\text{O}$, $\text{H}_2\text{C} > \text{C}(\text{CH}_3) = \text{CH.CO.CH}_3$, is a colorless oil, smelling like peppermint, and boiling at 130°C . (266°F .). Treated with phosphorus pentachloride, it is converted into the chloride, $\text{C}_4\text{H}_5\text{OCl}_2$. By boiling with dilute sulphuric acid, it is resolved into two molecules of acetone.

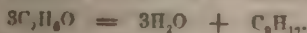
An isomeric compound, called *Metaacetone*, is formed by distilling sugar with lime; it is a liquid boiling at 84°C . (183.2°F .).

Phorone, $\text{C}_6\text{H}_{12}\text{O}$, probably $\text{H}_2\text{C} > \text{C}(\text{CH}_3) = \text{CH} - \text{C} \begin{array}{l} \nearrow \text{CH} - \text{CO} - \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$.—This body crystallizes in large yellowish prisms, melts at 28°C . (82.4°F .), boils at 196°C . (384.8°F .), and when boiled with dilute sulphuric acid takes up water, and is resolved into 3 molecules of acetone:



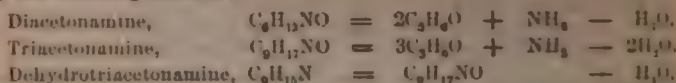
Acetophorone, produced by heating acetone with quick lime, and camphorone, obtained from camphoric acid, appear to be isomeric with the phorone obtained as above.

Acetone heated with strong sulphuric acid yields a distillate of mesitylene or trimethylbenzene, a body belonging to the aromatic group:



The same body is formed by the action of sulphuric acid on phorone. Other ketones heated with sulphuric acid likewise yield derivatives of benzene.

Acetonamines.*—Acetone, heated with ammonia, yields a mixture of three bases, the composition and mode of formation of which are indicated by the following formulæ:



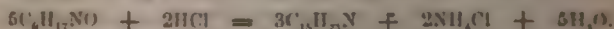
Diacetoneamine is the chief product obtained at a moderate heat, and is best prepared by passing dry ammonia gas into a flask containing acetone in a state of gentle ebullition. It is a colorless liquid, having an ammoniacal odor and strong alkaline reaction; mixes in all proportions with water, alcohol, and ether, oxidizes and turns brown on exposure to the air; forms crystalline salts with hydrochloric, sulphuric, and oxalic acids: the *platinochloride*, $2(\text{C}_6\text{H}_{13}\text{NO} \cdot \text{HCl}) \cdot \text{PtCl}_6$, crystallizes from water in orange-yellow monoclinic prisms containing 2 molecules H_2O .

Triacetoneamine, $\text{C}_9\text{H}_{17}\text{NO}$, is the chief product obtained at higher temperatures, and is best prepared by boiling diacetoneamine with acetone in a flask fitted with a reversed condenser. It crystallizes in large colored square tablets or long needles, having a faint ammoniacal and camphoraceous odor, and melting at 39.6°C . (103.3°F). It dissolves easily in water, alcohol, and ether; the aqueous solution has a strong alkaline reaction. It may be partly volatilized without decomposition at 100° , but decomposes at higher temperatures. The *hydrochloride*, $\text{C}_9\text{H}_{17}\text{NO} \cdot \text{HCl}$, crystallizes from alcohol in small needles. The *platinochloride*, $2(\text{C}_9\text{H}_{17}\text{NO} \cdot \text{HCl}) \cdot \text{PtCl}_6 + 4\text{H}_2\text{O}$, forms tufts of long golden-yellow needles, easily soluble in water, sparingly in alcohol.

An uncrystallizable modification of triacetoneamine, called *isotriacetoneamine*, is contained in the mixture of bases formed by the action of ammonia on acetone. It forms a crystalline *platinochloride* containing $2\text{H}_2\text{O}$.

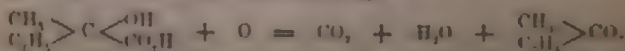
Dehydrotriacetoneamine, $\text{C}_9\text{H}_{15}\text{N}$, is obtained by distilling the last mother-liquor of the same crude product with potash; it forms a platinum salt, $2(\text{C}_9\text{H}_{15}\text{N} \cdot \text{HCl}) \cdot \text{PtCl}_6$, which crystallizes in oblique rhombic prisms.

Dehydropentacetoneamine, $\text{C}_{15}\text{H}_{27}\text{N}$, is obtained, amongst other products, by heating triacetoneamine with hydrochloric acid:



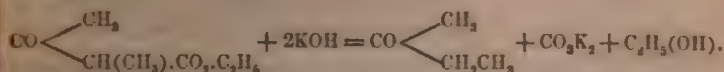
The hydrochloride forms small colorless crystals, slightly soluble in water. The free base separates as an oil on adding an alkali to the solution of the hydrochloride.

Methyl-ethyl Ketone. $\text{C}_4\text{H}_8\text{O} = \text{CO} < \begin{smallmatrix} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{smallmatrix}$, is formed: 1. By oxidation of secondary butyl alcohol. 2. By the action of zinc chloride on acetyl chloride, or of zinc-methyl on propionyl chloride. 3. By heating a mixture of propionic and acetic acid of calcium. 4. By oxidation of methyl-ethyl-oxalic acid (see *OXALIC ACID*):



* Heinrich, Liebig's Annalen, cxxxix. 177; cxxxviii. 305, 329; cxxxviii. 379, 388. Sokoloff and Latschnoff - *Deut. Chem. Ges. Ber.* vii. 1254.

5. By the action of alkalis on ethylic aceto-acetate (see CARBOKETONIC ACIDS):

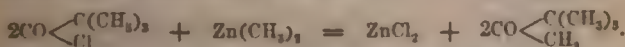


It is a fragrant liquid, of specific gravity 0.812 at 13° C. (55.4° F.), boiling at 81° C. (177.8° F.); unites with acid sulphites of alkali-metals; yields by oxidation two molecules of acetic acid.

The higher members of the series admit of isomeric modifications, the formula, $\text{C}_n\text{H}_{2n}\text{O}$, including three, and $\text{C}_6\text{H}_{12}\text{O}$, six isomeric ketones.

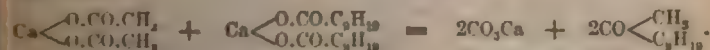
The table (p. 682) exhibits the specific gravities, boiling points, and products of oxidation of the best known ketones of the series.

Methyl-katabutyl Ketone, $\text{CH}_3\text{—CO—C}(\text{CH}_3)_3$, is probably the compound called pinacolin, formed by heating pinacone, $\text{C}_6\text{H}_{14}\text{O}_2$ (p. 608), with hydrochloric or dilute sulphuric acid. It is likewise formed by the action of zinc-methyl on trimethacetyl chloride:



Nascent hydrogen converts it into pinacolyl alcohol or methyl-katabutyl carbinol, $\text{C}(\text{CH}_3)_3\text{—CH(OH)—CH}_3$ (p. 589).

Methyl-nonyl Ketone, $\text{CH}_3\text{—CO—C}_9\text{H}_{19}$, is the chief constituent of oil of rue, and may be extracted therefrom by agitation with acid sodium sulphite. It is formed artificially by distilling a mixture of calcium acetate and rutate:



It is an oily liquid, with a bluish fluorescence, solidifying at low temperatures to a laminar mass.

| KETONES. | Boiling point. | Specific gravity. | Product oxidized. |
|---|----------------------------------|-----------------------------------|------------------------------|
| Dimethyl ketone,
$C_4H_8O = CO \begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}$ | 58° C.
(136.4° F.) | 0.814 at 6° C.
(42.8° F.) | Formic acids. |
| Methyl-ethyl ketone,
$C_5H_{10}O = CO \begin{smallmatrix} CH_3 \\ C_2H_5 \end{smallmatrix}$ | 51° C.
(117.8° F.) | 0.812 at 13° C.
(55.4° F.) | Acetic acid. |
| <i>Ketones, $C_5H_{10}O$:</i> | | | |
| 1. Methyl-propyl ketone,
$CO \begin{smallmatrix} CH_3 \\ (CH_2)_2(C_2H_5) \end{smallmatrix}$ | 90-101° C.
(210.2-213.8° F.) | 0.807 at 18° C.
(64.4° F.) | Acetic and
nic acids. |
| 2. Methyl-isopropyl ketone,
$CO \begin{smallmatrix} CH_3 \\ CH(C_2H_5)_2 \end{smallmatrix}$ | 93.5° C.
(200.3° F.) | 0.810 at 13° C.
(55.4° F.) | |
| 3. Diethyl ketone or propione,
$CO \begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix}$ | 101° C.
(213.8° F.) | 0.813 at 20° C.
(68° F.) | Acetic and
nic acids. |
| <i>Ketones, $C_6H_{12}O$:</i> | | | |
| 1. Methyl-butyl ketone,
$CO \begin{smallmatrix} CH_3 \\ (CH_2)_3(C_2H_5) \end{smallmatrix}$ | 127° C.
(260.6° F.) | 0.820 at 0° C. | Acetic and
acids. |
| 2. Methyl-isobutyl ketone,
$CO \begin{smallmatrix} CH_3 \\ CH_2CH(CH_3)_2 \end{smallmatrix}$ | 114° C.
(237.2° F.) | 0.819 at 0° C. | Acetic and
tyric acid. |
| 3. Methyl-katabutyl ketone,
$CO \begin{smallmatrix} CH_3 \\ C_3H_7 \end{smallmatrix}$ | 100° C.
(222.2° F.) | 0.823 at 0° C. | Acetic and
thylacetic. |
| 4. Ethyl-propyl ketone,
$CO \begin{smallmatrix} C_2H_5 \\ (CH_2)_2(C_2H_5) \end{smallmatrix}$ | 128° C.
(262.4° F.) | 0.833 at 0° C. | |
| <i>Ketones, $C_7H_{14}O$:</i> | | | |
| 1. Dipropyl ketone,
$CO \begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix}$ | 144° C.
(291.2° F.) | 0.82 at 20° C.
(68° F.) | Butyric and
pionic acids. |
| 2. Di-isopropyl ketone,
$CO \begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix}$ | 123-124° C.
(253.4-255.2° F.) | | Isobutyric
acetic acid. |
| 3. Diethylacetone,
$CO \begin{smallmatrix} CH_3 \\ CH(C_2H_5)_2 \end{smallmatrix}$ | 137-139° C.
(278.6-282.2° F.) | 0.817 at 22° C.
(71.6° F.) | |
| 4. Methyl-pentyl ketone,
$CO \begin{smallmatrix} CH_3 \\ C_4H_9 \end{smallmatrix}$ | 155-156° C.
(311-312.8° F.) | 0.813 at 20° C.
(68° F.) | Acetic and
valeric. |
| Methyl-hexyl ketone,
$C_8H_{16}O = CO \begin{smallmatrix} CH_3 \\ C_5H_{11} \end{smallmatrix}$ | 171° C.
(339.8° F.) | 0.818. | Acetic and
acids. |
| Di-isobutyl ketone or valerone,
$C_8H_{16}O = CO(C_3H_7)_2$ | 182° C.
(359.6° F.) | 0.833 at 20° C.
(68° F.) | |
| <i>Ketones, $C_{11}H_{22}O$:</i> | | | |
| 1. Diamyl ketone or caprone,
$CO(C_5H_{11})_2$ | 220° C.
(428° F.) | | |
| 2. Methyl-nonyl ketone,
$CO \begin{smallmatrix} CH_3 \\ C_8H_{17} \end{smallmatrix}$ | 225° C.
(437° F.) | Melting point,
15° C. (59° F.) | Acetic and
gouic acids. |
| Di-hexyl ketone or cenanthone,
$C_{13}H_{26}O = CO(C_5H_{11})_2$.. | 255° C.
(491° F.) | 30° C.
(86° F.) | |
| Diheptyl ketone,
$C_{15}H_{30}O = CO(C_7H_{15})_2$.. | 280° C.
(536° F.) | 40° C.
(104° F.) | |
| Dinonyl ketone,
$C_{19}H_{38}O = CO(C_9H_{19})_2$.. | 350° C.
(662° F.) | 58° C.
(130.4° F.) | |

ORGANIC ACIDS.

Organic acids, or Carbon-acids, contain the univalent group, COOH or $-\text{OH}$ (called carboxyl or oxetyl), linked by its free combining with a hydrocarbon residue, and they may be regarded as derived from hydrocarbons, saturated or unsaturated, by the substitution of one or more of these univalent groups for an equal number of hydrogen-atoms;

| | | | |
|--------------------------------|--|-----|--|
| from CH_4 are derived | $\text{CH}_3-\text{CO}_2\text{H}$ | and | $\text{CH}_2\begin{matrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{matrix}$ |
| Methane. | Acetic acid. | | Malonic acid. |
| " C_2H_6 " | $\text{C}_2\text{H}_5\cdot\text{CO}_2\text{H}$ | " | $\text{C}_2\text{H}_4\begin{matrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{matrix}$ |
| Ethane. | Propionic acid. | | Succinic acid. |
| " C_3H_8 " | $\text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}$ | " | $\text{C}_3\text{H}_6\begin{matrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{matrix}$ |
| Propane. | Crotonic acid. | | Citraconic acid. |

Organic acids are formed by oxidation from primary alcohols, the H_2 of the CH_2OH in these alcohols being replaced by O ; thus:

| Alcohols. | Acids. |
|-------------------------|------------------------|
| CH_3 | CH_3 |
| CH_2 | CH_2 |
| CH_2OH | COOH |
| Propyl alcohol. | Propionic acid. |
| CH_2OH | CH_2OH |
| CH_2 | CH_2 |
| CH_2OH | COOH |
| β Propene glycol. | β Lactic acid. |
| CH_2OH | CH_2OH |
| CHOH | CHOH |
| CH_2OH | COOH |
| Glycerin. | Glyceric acid. |
| | Oxymalonic acid. |

an acid may, however, contain one or more hydroxyl groups not directly attached with the group CO , and the hydrogen in these groups, as well as the group CO_2H , is replaceable by alcohol-radicles (also by alkalis) producing acid ethers, or alcoholic acids, *e. g.*, ethyl-lactic acid, $(\text{C}_2\text{H}_5)_2\text{CH}-\text{CO}_2\text{H}$.

The total number of hydroxyl groups in an organic acid is the same as of the alcohol from which it is derived, and this determines the acidity of the acid, and the number of ethers which it is capable of forming with any given alcohol-radicles; thus β -lactic acid, though it contains only one atom of basic hydrogen, and therefore forms only one class of salt, represented by the formula $\text{C}_3\text{H}_5\text{O}_3\text{M}$, is diatomic, like propylene-glycol, and can form two ethylic ethers, *viz.*, ethyl- β -lactic acid or ethyl- β -lactate or ethylic ethyl-lactate; thus:

| | | |
|------------------------|------------------------------------|------------------------------------|
| CH_2OH | $\text{CH}_3\text{OC}_2\text{H}_5$ | $\text{CH}_2\text{OC}_2\text{H}_5$ |
| CH_2 | CH_2 | CH_2 |
| COOH | COOH | COOC_2H_5 |
| β -Lactic acid | Ethyl- β -lactic | Diethylic |
| (monobasic). | acid (mono- | β -lactate |
| | basic). | (neutral). |

From these considerations it appears that monatomic acids must necessarily be monobasic, but diatomic acids may be either monobasic or tetrabasic; triatomic acids, either monobasic, bibasic, or tribasic, and so on.

Many of the most important acids are derived, in the manner above explained, from actually known alcohols; others, though they have no alcohols actually corresponding with them, are homologous with other acids derived from known alcohols; but there is also a considerable number of acids, especially those formed in the vegetable or animal organism, which cannot be regarded as derivatives of alcohols of any known series; but the number of these unclassified acids will doubtless diminish as their composition and reactions become more thoroughly known.

Acids may also be regarded as compounds of hydroxyl with oxygenated radicals (acid radicals) formed from the corresponding alcohol-radicals by substitution of O for H₂; e. g.,

| | | |
|-----------------------------------|---------------------------------|------------------------------------|
| $C_2H_5.OH$
Ethyl alcohol. | $C_2H_3O.OH$
Acetic acid. | |
| $C_3H_6(OH)_2$
Propene glycol. | $C_3H_4O(OH)_2$
Lactic acid. | $C_3H_2O_7(OH)_2$
Malonic acid. |

The replacement of the hydroxyl in an acid by chlorine, bromine, or iodine, gives rise to acid chlorides, etc.; thus from acetic acid, $C_2H_3O(OH)$, is derived acetic chloride, C_2H_3OCl , etc. The replacement of the hydrogen within the radicle (radical hydrogen) by the same elements, or by the groups, CN, NO₂, NH₂, etc., gives rise to chlorinated, brominated, cyanated, nitrated, and amidated acids. Lastly, the replacement of the *extra carbon* or *typic* hydrogen by alcohol-radicles gives rise to ethereal salts of compound ethers; and its replacement by acid radicles yields acid oxides or anhydrides (p. 481). The derivatives of each acid will be described in connection with the acid itself.

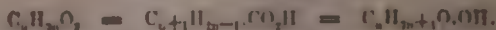
Monatomic Acids.

These acids, being derived from monatomic alcohols by substitution of O for H₂, necessarily contain two atoms of oxygen. Each series of hydrocarbons yields a series of monatomic alcohols and a series of monatomic acids; thus:

| Hydrocarbons. | Alcohols. | Acids. |
|---------------|----------------|------------------|
| C_nH_{2n+2} | $C_nH_{2n+2}O$ | $C_nH_{2n}O_2$ |
| C_nH_{2n} | $C_nH_{2n}O$ | $C_nH_{2n-2}O_2$ |
| C_nH_{2n-2} | $C_nH_{2n-2}O$ | $C_nH_{2n-4}O_2$ |
| C_nH_{2n-4} | $C_nH_{2n-4}O$ | $C_nH_{2n-6}O_2$ |
| etc. | etc. | etc. |

The best known monatomic acids are those belonging to the series $C_nH_{2n}O_2$, $C_nH_{2n-2}O_2$, $C_nH_{2n-4}O_2$, and $C_nH_{2n-6}O_2$. The last two belong to the aromatic group. Of the other series only a few terms have hitherto been obtained.

1. Acids of the Fatty Series.

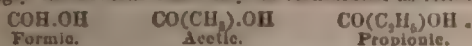


These acids are called *Fatty* or *Adipic* Acids, because most of them are of an oily consistence, and the higher members of the series are solid fats. The following is a list of the known members of the series:

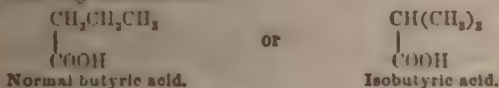
| | | | |
|---------------------------------|--|--------------------------|--|
| Formic acid | CH_3O_2 | Lauric acid | $\text{C}_{12}\text{H}_{24}\text{O}_2$ |
| Acetic acid | $\text{C}_2\text{H}_4\text{O}_2$ | Myristic acid | $\text{C}_{14}\text{H}_{28}\text{O}_2$ |
| Propionic acid | $\text{C}_3\text{H}_6\text{O}_2$ | Palmitic acid | $\text{C}_{16}\text{H}_{32}\text{O}_2$ |
| Butyric acid (normal) | $\text{C}_4\text{H}_8\text{O}_2$ | Margaric acid | $\text{C}_{17}\text{H}_{34}\text{O}_2$ |
| Valeric acid " | $\text{C}_5\text{H}_{10}\text{O}_2$ | Stearic acid | $\text{C}_{18}\text{H}_{36}\text{O}_2$ |
| Caproic acid " | $\text{C}_6\text{H}_{12}\text{O}_2$ | Arachidic acid | $\text{C}_{20}\text{H}_{40}\text{O}_2$ |
| Heptanthylic acid | $\text{C}_7\text{H}_{14}\text{O}_2$ | Behenic acid | $\text{C}_{22}\text{H}_{44}\text{O}_2$ |
| Caprylic acid | $\text{C}_8\text{H}_{16}\text{O}_2$ | Cerotic acid | $\text{C}_{27}\text{H}_{54}\text{O}_2$ |
| Pelargonic acid | $\text{C}_9\text{H}_{18}\text{O}_2$ | Melissic acid | $\text{C}_{30}\text{H}_{60}\text{O}_2$ |
| Butio or Capric acid | $\text{C}_{10}\text{H}_{20}\text{O}_2$ | | |

The higher members, from valeric acid upwards, are sometimes denoted by names indicating their number of carbon-atoms, and the alcohols from which they are derived, *e. g.*, *pentoic*, *hexoic*, *heptoic*, etc.

The acid radicals in the formula $\text{C}_n\text{H}_{2n-1}(\text{OH})$ may be regarded as compounds of carbonyl CO, with alcohol-radicals: $\text{C}_n\text{H}_{2n-1}\text{O} = \text{CO}(\text{C}_{n-1}\text{H}_{2n-1})$, and accordingly the several acids may be formulated as follows:—



All the acids of the series containing more than three carbon-atoms admit of isomeric modifications, according to the constitution of the alcohol-radicles which they contain: butyric acid, $\text{C}_4\text{H}_8\text{O}_2$, for example, may exhibit the following modifications:—

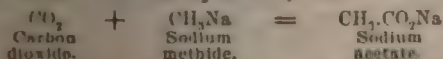


But none of these acids can exhibit modifications analogous to the secondary and tertiary alcohols: because in them the carbon-atom which is associated with hydroxyl has two of its other units of equivalence satisfied by an atom of bivalent oxygen, and therefore cannot unite directly with more than one other atom of carbon. Accordingly, it is found that the secondary and tertiary alcohols are not converted by oxidation into acids containing the same number of carbon-atoms as themselves.

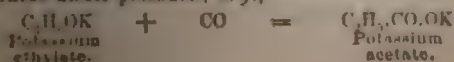
Occurrence.—Most of the fatty acids are found in the bodies of plants or animals, some in the free state; formic acid in ants and nettles; valeric acid in valerian root; pelargonic acid in the essential oil of *Pelargonium graveolens*, and cerotic acid in beeswax. Others occur as ethereal salts of ammonium or polyatomic alcohols: as cetyl palmitate in spermaceti; ceryl acetate in Chinese wax; glyceric butyrate, palmitate, stearate, etc., in natural fats.

Formation.—1. By oxidation of the primary alcohols of the methyl series, or by exposure to the air in contact with platinum black, or by heating with aqueous chromic acid.—2. By the oxidation of aldehydes. In this case, an atom of oxygen is simply added; *e. g.*, $\text{C}_2\text{H}_4\text{O}$ (aldehyde) + O = $\text{C}_2\text{H}_4\text{O}_2$ (acetic acid).

3. By the action of carbon dioxide on the potassium or sodium compound of an alcohol-radicle of the methyl series; thus:—

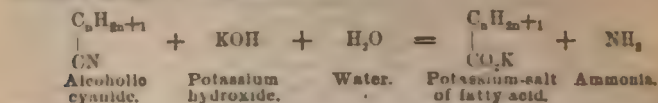


4. By heating the ethylate of an alkali-metal in alcoholic solution with carbon monoxide under pressure; *e. g.*,

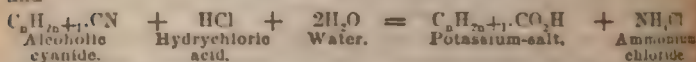


This reaction, however, is slow, and yields but a small product.

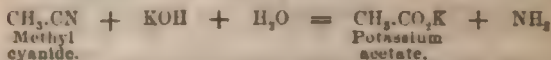
5. By the action of alkalis or acids on the cyanides of the alcohol-radicles, C_nH_{2n+1} ; thus:—



and



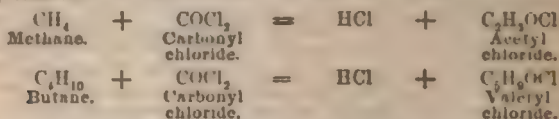
In this manner the cyanide of each alcohol-radicle yields the potassium-salt of the acid next higher in the series, that is, containing one atom of carbon more; methyl cyanide, for example, yielding acetic acid, ethyl cyanide yielding propionic acid, etc.; thus:—



6. By the action of water on the corresponding acid chlorides: *e. g.*,

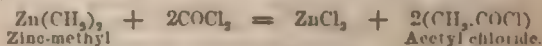


Now, these acid chlorides can be produced, in some instances at least, by the action of carbonyl chloride (phosgene gas) on the corresponding paraffins; thus:—

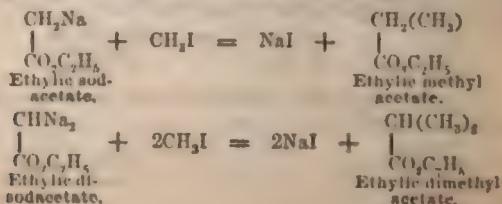


By these combined reactions, therefore, the paraffins may be converted into the corresponding fatty acids.

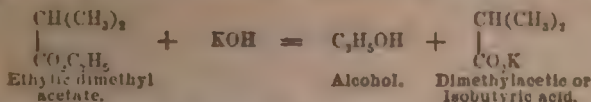
7. By the action of phosgene on the zinc-compounds of the alcohol-radicles, whereby acid chlorides are formed, to be subsequently decomposed by water:



8. By dissolving sodium in methylic or ethylic acetate, adding the iodide of an alcohol radicle, heating the mixture to 100° and distilling. The reaction, which is complex, and will be more fully explained hereafter (see CARBO-KETONIC ACIDS), may be viewed—so far as our present purpose is concerned—as consisting in the substitution of 1 or 2 atoms of sodium for hydrogen in the methyl-group of acetic acid, and the decomposition of the resulting compound by the alcoholic iodide: *e. g.*,



The resulting ethers saponified with caustic potash yield the acids; thus:

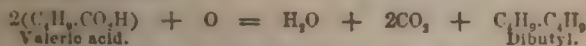


Ethyl-acetic or normal butyric acid, $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{—CO}_2\text{H}$, and other members of the series, may be obtained in a similar manner.

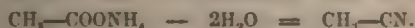
The eight modes of formation above given are general, or capable of being made so. There are also special methods of producing particular acids of the series, but in most of these cases the reactions cannot be distinctly traced; thus formic, acetic, propionic, butyric, and valeric acids are produced by the oxidation of albumin, fibrin, casein, gelatin, and other similar substances; propionic and butyric acids, in certain kinds of fermentation; acetic acid by the destructive distillation of wood and other vegetable substances.

Properties.—Most of the fatty acids are, at ordinary temperatures, transparent and colorless liquids; formic and acetic acids are watery; propionic acid and the higher acids, up to pelargonic acid, are oily; stearic acid and those above it are solid at ordinary temperatures, most of them being crystalline fats; cerotic and melissic acids are of waxy consistence.

Reactions.—1. When the fatty acids are submitted to the action of nascent oxygen evolved by electrolysis, the carboxyl (COOH) contained in them is resolved into water and carbon dioxide, and the alcohol-radicle is set free (p. 492); thus:

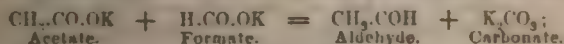


2. When the ammonium salt of either of these acids is heated with phosphoric oxide, it gives up water, and is converted into the cyanide of the alcohol-radicle next below it; e. g., ammonium acetate into methyl cyanide:



This reaction is the converse of the fifth mode of formation above given.

3. By distilling the potassium salt of a fatty acid with an equivalent quantity of potassium formate, the corresponding aldehyde is obtained:

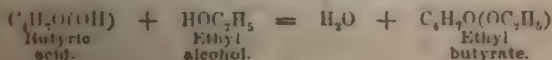


and the aldehyde, treated with nascent hydrogen, is converted into a primary alcohol (pp. 558, 565).

4. By subjecting the barium or calcium salt of a fatty acid to dry distillation, a similar decomposition takes place, resulting in the formation of a ketone; and the ketone, treated with nascent hydrogen, yields a secondary alcohol (pp. 558, 577).

By these reactions, the fatty acids may be converted into alcohols.

5. The fatty acids, heated with alcohols in sealed tubes, yield compound ethers, or ethereal salts, water being eliminated:



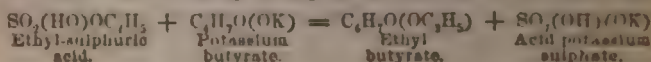
The conversion, however, is never complete, a portion, both of the acid

and of the alcohol, remaining unaltered, in whatever proportion they may be mixed (p. 553).

The ethereal salts of the fatty acids are, for the most part, more easily obtained by acting upon the alcohol with an acid chloride, or by passing hydrochloric acid gas into a solution of the fatty acid in the alcohol; thus butyric chloride and ethyl alcohol yield ethyl-butyrate:



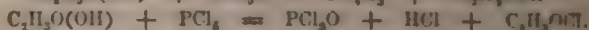
Another method very commonly adopted, is to distil a potassium salt of the fatty acid with a mixture of the alcohol and strong sulphuric acid. In this case an acid sulphuric ether is first formed (as ethyl-sulphuric acid from ethyl alcohol, p. 573), and this acts upon the salt of the fatty acid in the manner illustrated by the equation:



The ethereal salts of the fatty acids are either volatile, oily or syrupy liquids, or crystalline solids, for the most part insoluble in water, but soluble in alcohol and in ether. When distilled with potash or soda, they take up water and are saponified, that is to say, resolved into the alcohol and acid; e. g., ethyl butyrate into butyric acid and ethyl alcohol:

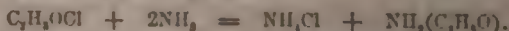


6. The fatty acids are strongly acted upon by the *chlorides, bromides, oxychlorides, and oxybromides of phosphorus*, yielding acid chlorides and bromides, the phosphorus being at the same time converted into phosphorous or phosphoric acid; thus:



These acid chlorides are, for the most part, oily liquids, having a pungent acid odor; they are easily decomposed by water, yielding the fatty acid and hydrochloric acid. This decomposition takes place also when they are exposed to the air: hence they emit dense acid fumes. They react in the exactly similar manner with alcohols, as above mentioned, yielding hydrochloric acid and a compound ether.

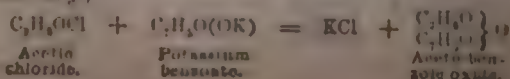
7. The chlorides of the acid radicles, $C_nH_{2n+1}O$, act violently on ammonia, forming ammonium chloride and the corresponding amides, acetyl chloride, for example, yielding acetamide:



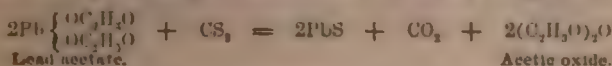
8. The acid chlorides, distilled with a metallic salt of the corresponding acid, yield a metallic chloride and the oxide or anhydride corresponding with the acid; thus:



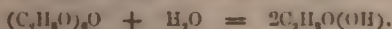
In like manner, when distilled with the potassium salt of another monatomic acid, they yield oxides or anhydrides containing two monatomic acid radicles: e. g.,



The oxides of the fatty acid radicles may also be prepared by heating a dry lead-salt of the acid, in a sealed tube with carbon bisulphide: *e. g.*,

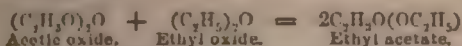


The oxides of the fatty acid radicles are gradually decomposed by water, quickly when heated, yielding two molecules of the corresponding acid:

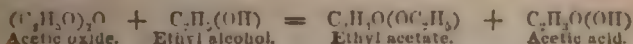


Those containing two acid radicles yield one molecule of each of the corresponding acids.

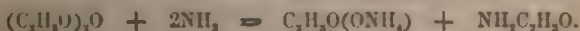
In contrast with *alcoholic oxides (oxygen-ethers)*, the acid oxides are converted into ethereal salts:



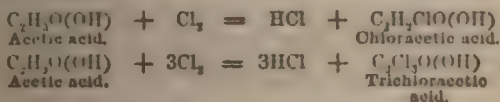
With *alcohols*, in like manner, they yield a mixture of a compound ether with the acid:



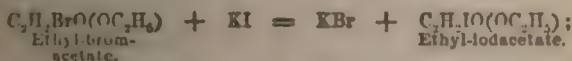
The acid oxides are decomposed by *ammonia gas*, yielding a mixture of an ammonium-salt with an amide; *e. g.*,



9. The fatty acids, subjected to the action of *chlorine* or *bromine*, give off hydrochloric or hydrobromic acid, and are converted into substitution-compounds containing one or more atoms of chlorine or bromine in place of hydrogen; but it is only the hydrogen within the radicle that can be thus exchanged, not that belonging to the hydroxyl group (the so-called *typic hydrogen*), so that the number of chlorine or bromine-atoms introduced in place of hydrogen is always less by at least one than the number of hydrogen-atoms in the acid:

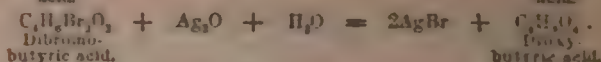
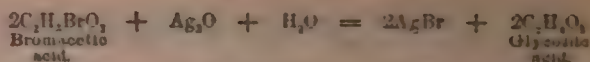


The iodated acids of the same series (or rather their ethereal salts) are obtained by heating the corresponding bromine-compounds with potassium iodide:



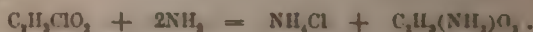
and the ethers treated with potash yield potassium salts of the iodated acids, from which the acids may be obtained by decomposition with sulphuric acid.

10. The chlorinated and brominated fatty acids, boiled with *water* and *silver oxide*, exchange the whole of their chlorine or bromine for an equivalent quantity of hydroxyl, producing new acids, which differ from the primitive acids by a number of atoms of oxygen equal to the number of atoms of chlorine or bromine present; *e. g.*,



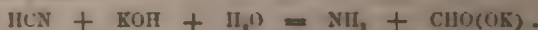
Dichloroacetic and trichloroacetic acid are not sufficiently stable to exhibit this transformation, their molecules splitting up altogether when treated with silver oxide.

11. The monochlorinated and monobrominated acids, subjected to the action of an alcoholic solution of *ammonia gas*, yield ammonium chloride and a new acid, in which the chlorine or bromine is replaced by ammonia. Thus monochloroacetic acid yields amidacetic acid, or glycocine:—

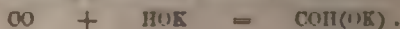


There is another way of viewing these amidated acids, which will be considered hereafter.

Formic Acid, $\text{CH}_2\text{O}_2 = \text{CHO}(\text{OH}) = \text{H.CO.OH}$.—This acid occurs in the concentrated state in the bodies of ants, in the hairs and other parts of certain caterpillars, and in stinging nettles. It may be produced by the first, second, and fourth of the above-mentioned general methods of forming the fatty acids—viz., by the slow oxidation of methyl alcohol, or of formic aldehyde, in contact with platinum black, and as a potassium salt by heating hydrocyanic acid (hydrogen cyanide) with an alcoholic solution of potash:—

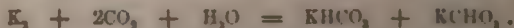


It is also produced by certain special reactions—viz., 1. By passing carbon monoxide over moist potassium hydroxide, the gas being thereby absorbed, and producing potassium formate:—

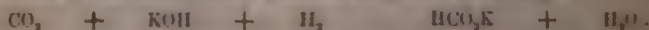


The absorption of the gas is accelerated by the presence of a considerable quantity of water, and still more by alcohol or ether.

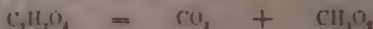
2. By passing carbon dioxide and water-vapor over potassium at a moderate heat, acid potassium carbonate, KHCO_3 , being formed at the same time:—



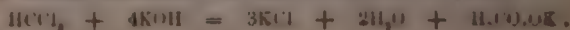
3. By the action of sodium-amalgam on a strong solution of ammonia carbonate, and by boiling zinc-dust (a mixture of metallic zinc, oxide, and hydrate), or zinc carbonate with potash solution. In both these cases the production of formic acid is due to the nascent hydrogen, which, in presence of the alkali, unites with the CO_2 of the carbonate:—



4. By distilling dry oxalic acid either alone or mixed with sand or pumice-stone, or better, with glycerin:—

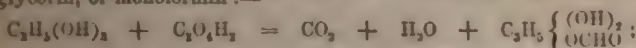


5. By boiling chloroform with alcoholic solution of potash:—

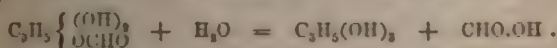


6. By the oxidation of sugar, starch, gum, and organic substances in general. This reaction affords a convenient method of preparing the acid: 1 part of sugar, 3 parts of manganese dioxide, and 2 parts of water, are mixed in a very capacious retort, or large metal still; 3 parts of oil of vitriol, diluted with an equal weight of water, are then added, and when the first violent effervescence from the disengagement of carbon dioxide has subsided, heat is cautiously applied, and a considerable quantity of liquid distilled over. This is very impure: it contains a volatile oily matter, and some substance which communicates a pungency not proper to formic acid in that dilute state. The acid liquid is neutralized with sodium carbonate, and the resulting formate purified by crystallization, and, if needful, by animal charcoal. From this or any other of its salts, solution of formic acid may be readily obtained by distillation with sulphuric acid.

The best mode of preparation, however, consists in heating oxalic acid in contact with glycerin. Very concentrated glycerin is added to crystallized oxalic acid, $C_2H_2O_4 + 2H_2O$, and the mixture is heated to 100° – 110° C. (212° – 230° F.), whereupon carbon dioxide escapes, and dilute formic acid distils over. As soon as the evolution of gas ceases, more oxalic acid is added, and the heating continued, whereupon a stronger formic acid distils over, and on further addition of oxalic acid, and heating, an acid of constant strength (56 per cent.) passes over. The course of the reaction is as follows: The crystallized oxalic acid, when heated, gives up its water, and the remainder fuses with the glycerin, the monoformic ether of glycerin, or monoformin:—



and the oxalic acid afterwards added is likewise resolved into anhydrous acid and water, which decomposes the formin into glycerin and formic acid:—



The regenerated glycerin reacts with the anhydrous oxalic acid, reproducing monoformin.

To obtain the acid in its most concentrated state, the dilute acid is saturated with lead oxide, the liquid is evaporated to complete dryness, and the dried lead formate, reduced to fine powder, is very gently heated in a glass tube connected with a condensing apparatus, through which a current of dry sulphuretted hydrogen gas is passed.

Pure anhydrous formic acid is a clear, colorless liquid, which fumes slightly in the air, has an exceedingly penetrating odor, boils at about 100° , and crystallizes in large brilliant plates when cooled below 0° . The specific gravity of the acid is 1.233. Its vapor is inflammable, and burns with a blue flame. Concentrated formic acid is extremely corrosive, attacking the skin, and forming a blister or an ulcer, painful and difficult to heal.

Formic acid mixes in all proportions with water, alcohol, and ether. The aqueous acid has an odor and taste much resembling those of acetic acid; it reddens litmus strongly, and decomposes alkaline carbonates with effervescence.

Formic acid also unites with water in definite proportion, forming a hydrate, $CH_2O_2 + H_2O$, which remains liquid at low temperatures, and dissolves at 100° C. (222.8° F.). This hydrate may be regarded as a triatomic acid, viz., orthoformic acid, $HC(OH)_2$.

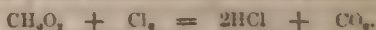
Formic acid is a powerful reducing agent. It may be readily distin-

* At 46.6° (Liebig); 100° (Persson); 101.1° (Roseoe); 106.6° (Kopp).

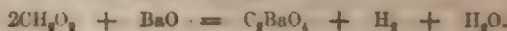
guished from acetic acid by heating it with solution of *silver nitrate*; the metal is thus reduced, sometimes in the pulverulent state, sometimes as a specular coating on the glass tube, and carbon dioxide is evolved. Mercuric chloride is reduced by formic acid to calomel.

Formic acid heated with *oil of vitriol* splits up into water and carbon monoxide, $\text{CH}_2\text{O}_2 = \text{H}_2\text{O} + \text{CO}$.

Chlorine converts it into hydrochloric acid and carbon dioxide:



Formic acid heated with strong *bases* is converted into oxalic acid, with disengagement of hydrogen; *e. g.*,



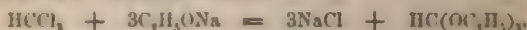
Formates.—The composition of these salts is expressed by the formulae, MCHO_2 , $\text{M}''(\text{CHO}_2)_2$, $\text{M}'''(\text{CHO}_2)_3$, etc., according to the equivalent value of the metal or other positive radicle contained in them. They are all soluble in water; their solutions form dark-red mixtures with *ferrous* salts. When distilled with strong sulphuric acid, they give off carbon monoxide and leave a residue of sulphate. The formates of the *alkali-metals* heated with the corresponding salts of other fatty acids, yield a carbonate and aldehyde (p. 665).

Sodium formate crystallizes in rhombic prisms containing $\text{CHO}_2\text{Na} \cdot 4\text{aq}$. It reduces many metallic oxides when fused with them. *Potassium formate*, CHO_2K , is difficult to crystallize, on account of its great solubility. *Ammonium formate* crystallizes in square prisms: it is very soluble, and is decomposed at high temperatures into hydrocyanic acid and water, the elements of which it contains: $\text{CHO}_2\text{NH}_4 = 2\text{H}_2\text{O} + \text{CNH}$. The formates of *barium*, *strontium*, *calcium*, and *magnesium* form small, prismatic, easily soluble crystals. *Lead formate* crystallizes in small, diverging, colorless needles, which require for solution 40 parts of cold water. The *manganous*, *ferrous*, *zinc*, *nickel*, and *cobalt formates* are also crystallizable. *Cupric formate* is very beautiful, crystallizing in bright blue rhombic prisms of considerable size. *Silver formate* is white, but slightly soluble, and decomposed by the least elevation of temperature.

Methyl formate, CHO_2CH_3 , metamerie with acetic acid, is prepared by heating in a retort equal weights of neutral methyl sulphate and sodium formate. It is a very volatile liquid, lighter than water, boiling between 36° and 38° C. (96.8° – 100.4° F.).

Ethyl formate, $\text{CHO}_2\text{C}_2\text{H}_5$, metamerie with methyl acetate and propionic acid (p. 484), is prepared by distilling a mixture of 7 parts of dry sodium formate, 10 of oil of vitriol, and 6 of strong alcohol. The formic ether, separated by the addition of water to the distilled product, is agitated with a little *magnesia*, and left for several days in contact with calcium chloride. Ethyl formate is colorless, has an aromatic odor, a density of 0.915, and boils at 56° C. (132.8° F.). Water dissolves it to a small extent.

Ethyl Orthoformate, $\text{HC}(\text{OC}_2\text{H}_5)_3$, is produced by heating chloroform with sodium ethylate in alcoholic solution:



It is a liquid having an aromatic odor, boiling at 146° C. (294.8° F.), insoluble in water. When heated with glacial acetic acid it is resolved into formate and acetate of ethyl.

Acetic acid. $C_2H_4O_2 = C_2H_3O(OH) = CH_3(COOH)$.—This acid is found in small quantities in the juices of plants and in animal fluids. It may be produced by either of the first seven general methods of formation given on pages 685–686, and in particular by the slow oxidation of alcohol. When spirit of wine is dropped upon platinum black, the oxygen condensed in the pores of the latter reacts so powerfully upon the alcohol as to cause its instant inflammation. When the spirit is mixed with a little water, and slowly dropped upon the finely divided metal, oxidation still takes place, but with less energy, and vapor of acetic acid is abundantly evolved. In all these modes of formation, the acetic acid is ultimately producible from inorganic materials. It is also formed by the action of nascent hydrogen on trichloroacetic acid, which may itself be produced from inorganic materials. Lastly, acetic acid is obtained, together with many other products, in the destructive distillation of wood and other vegetable substances.

Preparation.—1. Dilute alcohol, mixed with a little yeast, or almost any acidized organic matter susceptible of putrefaction, and exposed to the air, speedily becomes oxidized to acetic acid. Acetic acid is thus manufactured in Germany, by suffering such a mixture to flow over wood shavings steeped in a little vinegar, contained in a large cylindrical vessel through which a current of air is made to pass. The greatly extended surface of the liquid expedites the change, which is completed in a few hours. No carbonic acid is produced in this reaction.

The best vinegar is made from wine by spontaneous acidification in a partially filled cask to which the air has access. Vinegar is first introduced into the empty vessel, and a quantity of wine added; after some days, a second portion of wine is poured in, and after similar intervals, a third and a fourth. When the whole has become vinegar, a quantity is drawn off equal to that of the wine employed, and the process is recommenced. The temperature of the building is kept up to $30^\circ C.$ ($86^\circ F.$). Such is the plan adopted at Orleans. In England vinegar is prepared from a kind of beer made for the purpose. The liquor is exposed to the air in half-empty casks, loosely stopped, until acidification is complete. Frequently a little sulphuric acid is afterwards added, with the view of checking further decomposition, or *mothering*, by which the product would be spoiled.

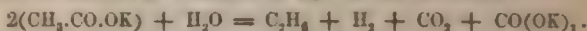
When dry, hard wood, as oak and beech, is subjected to destructive distillation at a red heat, acetic acid is found among the liquid condensable products of the operation. The distillation is conducted in a large iron cylinder, to which a worm or condenser is attached; a sour, watery liquid, a quantity of tar, and much inflammable gas pass over, while charcoal of excellent quality remains in the retort. The acid liquid is subjected to distillation, the first portion being collected apart for the preparation of wood-spirit. The remainder is saturated with lime, concentrated by evaporation, and mixed with the solution of sodium sulphate; calcium sulphate is thereby precipitated, while the acetic acid is transferred to the soda. The altered solution is evaporated to its crystallizing point; and the crystals are drained as much as possible from the dark, tarry mother-liquor, and deprived by heat of their combined water. The dry salt is then cautiously fused, by which the last portions of tar are decomposed or expelled: it is then redissolved in water, and recrystallized. Pure sodium acetate, thus obtained, readily yields acetic acid by distillation with sulphuric acid.

The strongest acetic acid is prepared by distilling finely powdered anhydrous sodium acetate with three times its weight of strong sulphuric acid. The liquid is purified by rectification to free it from sodium sulphate accidentally thrown up, and exposed to a low temperature. Crystals of pure

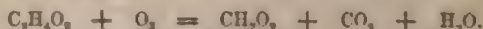
acetic acid, $C_2H_4O_2$, then form in large quantity: they may be drained from the weaker fluid portion, and suffered to melt. Below $15.5^\circ C.$ ($59.9^\circ F.$) this substance, often called *glacial acetic acid*, forms large, colorless, transparent crystals, which above that temperature fuse to a thin, colorless liquid, of exceedingly pungent and well-known odor; it raises blisters on the skin. It is miscible in all proportions with water, alcohol, and ether, and dissolves camphor and several resins. When diluted it has a pleasant acid taste. Glacial acetic acid in the liquid state has a density of 1.063, and boils at $120^\circ C.$ ($248^\circ F.$). Its vapor is inflammable, and exhibits the variations of density already noticed (p. 230). At $300^\circ C.$ ($572^\circ F.$), or above, it is 2.08 compared with air, or 30 compared with hydrogen, agreeing exactly with the theoretical density, which is half the molecular weight; but at temperatures near the boiling point it is considerably greater, being 2.90 at $140^\circ C.$ ($284^\circ F.$), and 3.20 at $125^\circ C.$ ($257^\circ F.$) (referred to air).

Dilute acetic acid, or distilled vinegar, used in pharmacy, should always be carefully examined for copper and lead; these impurities are contracted from the metallic vessel or condenser sometimes employed in the process. The strength of any sample of acetic acid cannot be safely inferred from its density, but it is easily determined by observing the quantity of dry sodium carbonate necessary to saturate a known weight of the liquid. Common vinegar contains from 5 to 15 per cent. of the pure acid.

Acetic acid exhibits all the reactions of the fatty acids in general (pp. 687-689). The acid itself does not readily conduct the electric current, but a solution of potassium acetate is decomposed by electrolysis, with formation of dimethyl, or ethane, and potassium carbonate:



Acetic acid is not attacked by nitric acid, but *periodic acid* converts it by oxidation into formic acid and carbon dioxide, being itself reduced to iodic acid or even to free iodine:



Potassium acetate distilled with *arsenious oxide* gives off a highly inflammable and characteristically fetid oil, consisting chiefly of *arsendimethyl*, or *cacodyl*, $As_2(CH_3)_4$.

Acetates.—Acetic acid forms a large number of highly important salts, represented by the formulæ, $MC_2H_3O_2$, $M''(C_2H_3O_2)_2$, or $M'''(C_2H_3O_2)_3$, according to the equivalent value of the metal contained in them. Being a monobasic acid, it cannot form any acid salts properly so called, that is, by replacement of a *part* of its typic hydrogen (p. 684); but the normal acetates of the alkali-metals can take up a molecule of acetic acid, just as they take up water of crystallization, forming salts called *acid acetates* or *diacetates*, $MC_2H_3O_2.C_2H_4O_2$. There are also *basic acetates*, formed by the union of a molecule of a normal acetate with a molecule of metallic oxide or hydrate.

POTASSIUM ACETATE.—The *normal salt*, $KC_2H_3O_2$, crystallizes with great difficulty: it is generally met with as a foliated, white, crystalline mass, obtained by neutralizing potassium carbonate with acetic acid, evaporating to dryness, and heating the salt to fusion. It is extremely deliquescent, and soluble in water and alcohol: the solution is usually alkaline, from a little loss of acid by the heat to which it has been subjected. From the alcoholic solution, potassium carbonate is thrown down by a stream of carbon dioxide.

The *acid salt*, $\text{KC}_2\text{H}_3\text{O}_2 \cdot \text{C}_2\text{H}_4\text{O}_2$, is formed by evaporating a solution of the neutral salt in excess of acetic acid, and crystallizes by slow evaporation in long flattened prisms. It is very deliquescent, and decomposes at 200°C . (392°F .), giving off crystallizable acetic acid.

SODIUM ACETATE, $\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{Aq}$.—The mode of preparation of this salt on the large scale has been already described: it forms large, transparent, colorless crystals, derived from a rhombic prism, which are easily rendered anhydrous by heat, effloresce in dry air, and dissolve in 3 parts of cold, and in an equal weight of hot water; it is also soluble in alcohol. The taste of this salt is cooling and saline. The dry salt melts at 288°C . (550.4°F .), and begins to decompose at 315°C . (599°F .).

AMMONIUM ACETATES.—The *neutral acetate*, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, is a white odorless salt, obtained by saturating glacial acetic acid with dry ammonia gas. It is very difficult to obtain in the crystalline form, for its aqueous solution, when evaporated, gives off ammonia, and leaves the acid salt. When distilled with phosphoric oxide, it loses 2 molecules of water, and gives off ethenyl nitril or acetonitril, $(\text{C}_2\text{H}_3)\text{N} = \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 - 2\text{H}_2\text{O}$. The aqueous solution, known in the Pharmacopœia as *Spiritus Mindereri*, is prepared by saturating aqueous acetic acid with ammonia or ammonium carbonate.

The *acid salt*, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot \text{C}_2\text{H}_4\text{O}_2$, is obtained as a crystalline sublimate by heating powdered sal-ammoniac with potassium or calcium acetate, ammonia being given off at the same time; also as a radiated crystalline mass by evaporating the aqueous solution of the neutral salt.

The acetates of *barium*, *strontium*, and *calcium* are very soluble, and can be procured in crystals: *magnesium acetate* crystallizes with difficulty.

ALUMINIUM ACETATES.—The neutral salt, $\text{Al}_2(\text{C}_2\text{H}_3\text{O}_2)_6$, is very soluble in water, and dries up in the vacuum of the air-pump to a gummy mass without trace of crystallization. If foreign salts are present, the solution of the acetate becomes turbid on heating, from the separation of a basic compound, which redissolves as the liquid cools. Aluminium acetate is much employed in calico printing: it is prepared by mixing solutions of lead acetate and alum, and filtering from the insoluble lead sulphate. The liquid is thickened with gum or other suitable material, and with it the design is impressed upon the cloth by a wood-block, or by other means. Exposure to a moderate degree of heat drives off the acetic acid, and leaves the alumina in a state capable of entering into combination with the dye-stuff.

Some very interesting researches on aluminium acetate have been published by the late Mr. Walter Crum.* The solution obtained by decomposing aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$, with lead acetate, may be supposed to contain neutral aluminium acetate, $(\text{Al}_2)(\text{C}_2\text{H}_3\text{O}_2)_6$, or $\text{Al}_2\text{O}_3 \cdot 3\text{C}_2\text{H}_4\text{O}_2$. This salt cannot, however, be obtained in the dry state. If the solution be rapidly evaporated at low temperatures, by being spread in thin layers on glass or porcelain, a basic soluble acetate is obtained, having the composition $\text{Al}_2\text{O}_3 \cdot 2\text{C}_2\text{H}_4\text{O}_2 + 4\text{Aq}$; but if the solution be left to stand in the cold, or submitted to the action of heat, insoluble basic salts are precipitated, differing in composition from the former by containing in the first case five, and in the second two, molecules of water instead of four.

The soluble aluminium acetate, when exposed in a dilute solution to the temperature of boiling water for several days, undergoes a very remarkable change, the whole, or nearly the whole, of the acetic acid being expelled by the action of heat, and a peculiar soluble modification of

* Chem. Soc. Quar. Journ., vi 216.

alumina (already described under ALUMINUM, p. 341), remaining in solution.

Manganese acetate forms colorless, rhombic, prismatic crystals, permanent in the air. *Ferric acetate* crystallizes in small, greenish-white masses, very prone to oxidation; both salts dissolve freely in water. *Ferric peroxide* is a dark, brownish-red, uncrystallizable liquid, of powerful astringent taste. *Cobalt acetate* forms a violet-colored, crystalline, deliquescent mass. The *nickel salt* separates in green crystals, which dissolve in 6 parts of water.

LEAD ACETATES.—The *normal salt*, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{Aq.}$, is prepared on a large scale by dissolving litharge in acetic acid; it may be obtained as colorless, transparent, prismatic crystals, but is generally met with as commences as a confusedly crystalline mass, somewhat resembling loaf-sugar. From this circumstance and from its sweet taste, it is often called *rose of lead*. The crystals are soluble in about $1\frac{1}{4}$ parts of cold water, effervesce in dry air, and melt when gently heated in their water of crystallization; this water is easily driven off, and the anhydrous salt obtained, which melts, and afterwards decomposes, at a high temperature. Acetate of lead is soluble in alcohol. The aqueous solution has an intensely sweet, and at the same time, astringent taste, and is not precipitated by ammonia. It is an article of great value to the chemist.

Basic Acetates (Subacetates) of Lead.—A *sesquibasic acetate*, $2\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO}$, is produced when the neutral anhydrous salt is so far decomposed by heat as to become converted into a porous white mass, decomposable only at a much higher temperature. It is soluble in water and separates from the solution evaporated to a syrupy consistence in the form of crystalline scales. A *tripbasic acetate*, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbO}$, is obtained by digesting, at a moderate heat, 7 parts of finely powdered litharge, 6 parts of lead acetate, and 30 parts of water; or, by mixing a cold saturated solution of neutral lead acetate with a fifth of its volume of caustic ammonia, and leaving the whole for some time in a covered vessel. The salt separates in minute needles containing one molecule of water. The solution of basic acetate prepared by the first method is known in pharmacy under the name of *Goulard water*. There is also a *sesquibasic oxide*, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 5\text{PbO}$, formed by adding a great excess of ammonia to a solution of normal lead acetate, or by digesting the normal salt with a large quantity of oxide. It is a white, slightly crystalline substance, insoluble in cold, and but little soluble in boiling water. The solutions of the basic lead acetates have a strong alkaline reaction, and absorb carbonic acid with the greatest avidity, becoming turbid from precipitation of basic carbonate.

CUPRIC ACETATES.—The *normal acetate*, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Aq.}$, is prepared by dissolving *verdigris* in hot acetic acid, and leaving the filtered solution to cool. It forms beautiful dark-green crystals, which dissolve in 14 parts of cold and 5 parts of boiling water, and are also soluble in alcohol. A solution of this salt, mixed with sugar and heated, yields cupric oxide in the form of minute red octohedral crystals; the residual copper solution is not precipitated by an alkali. Cupric acetate yields, by destructive distillation, strong acetic acid containing acetone and contaminated with copper. The salt is sometimes called *distilled verdigris*, and is used as a pigment.

Basic Cupric Acetates.—Common *verdigris*, made by exposing plates of copper to the air for several weeks, in contact with acetic acid or

The juice of grapes, is a mixture of several basic cupric acetates, which have a green or blue color. One of these, $2\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{CuO} + 6\text{Aq.}$, is obtained by digesting the powdered verdigris in warm water, and leaving the soluble part to spontaneous evaporation. It forms a blue, crystalline mass, but little soluble in cold water. When boiled, it deposits a brown powder, which is a subsalt with large excess of base. The green insoluble residue of the verdigris contains $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{CuO} + 3\text{Aq.}$; it may be formed by digesting normal cupric acetate with the hydrated oxide. By boiling with water it is resolved into normal acetate and the brown basic salt.

SILVER ACETATE, $\text{AgC}_2\text{H}_3\text{O}_2$, is obtained by mixing potassium acetate with silver nitrate, and washing the precipitate with cold water to remove the potassium nitrate. It crystallizes from a warm solution in small colorless needles, which have but little solubility in the cold.

Mercurous acetate forms small scaly crystals, which are as feebly soluble as those of acetate of silver. *Mercuric acetate* dissolves with facility.

METHYL ACETATE, $\text{CH}_3 \cdot \text{C}_2\text{H}_3\text{O}_2$, occurs in crude wood-spirit. It is prepared by distilling 2 parts of methyl alcohol with 1 part of glacial acetic acid and 3 part of sulphuric acid, or 1 part of methyl alcohol with 1 part of potassium acetate and 2 parts of sulphuric acid. When purified by rectification over calcium chloride and quick-lime, it forms a colorless fragrant liquid, of sp. gr. 0.9562 at 0° , boiling at 55° or 56°C. (131° – 132.8°F.). It dissolves in water, and mixes in all proportions with alcohol and ether.

ETHYL ACETATE, $\text{C}_2\text{H}_5 \cdot \text{C}_2\text{H}_3\text{O}_2$, may be prepared by heating together in a retort, 3 parts of potassium acetate, 3 parts of strong alcohol, and 2 parts of oil of vitriol. The distilled product is mixed with water, to separate the alcohol, digested first with a little chalk, and afterwards with fused calcium chloride, and, lastly, rectified. The pure ether is an exceedingly fragrant limpid liquid, having a density of 0.9105 at 0° , 0.9068 at 15°C. (59°F.), and boiling at 77°C. (170.6°F.). Alkalies decompose it in the manner already mentioned (p. 688). When treated with ammonia, it yields *acetamide*, $\text{NH}_2 \cdot \text{C}_2\text{H}_3\text{O}$.

On the reaction of ethyl acetate and homologous ethers with sodium and the iodides of alcohol-radicles, see p. 686; also **CARBOKETONIC ACIDS**.

AMYL ACETATE, $\text{C}_5\text{H}_{11} \cdot \text{C}_2\text{H}_3\text{O}_2$, prepared in a similar manner from ordinary amyl alcohol, boils at 140°C. (284°F.). It possesses in a remarkable manner the odor of the Jargonelle pear, and is manufactured on a large scale for flavoring liquors and confectionery.

ETHENE ACETATES.—These compounds may be derived from ethene alcohol (glycol) by substitution of one or two equivalents of acetyl for hydrogen. The *monoacetate*, $(\text{C}_2\text{H}_4) \begin{Bmatrix} \text{OH} \\ \text{OC}_2\text{H}_3\text{O} \end{Bmatrix}$, is produced by heating ethene dibromide with an alcoholic solution of potassium acetate. The product is distilled, the portion coming over at 182°C. (359.6°F.) being kept separate. It is a colorless, oily liquid, miscible in every proportion with water or alcohol. Hydrochloric acid gas passed into ethene monoacetate converts it into ethene acetochloride, or glycollic chloroacetin, $\text{C}_2\text{H}_4 \begin{Bmatrix} \text{Cl} \\ \text{OC}_2\text{H}_3\text{O} \end{Bmatrix}$, which is precipitated, on addition of water, as an oily liquid boiling at 145°C. (293°F.). Treatment with potash decomposes it into ethene oxide, potassium acetate, and potassium chloride.

Ethene diacetate, $C_2H_4 \begin{Bmatrix} OC_2H_3O \\ OC_2H_3O \end{Bmatrix}$, is prepared by digesting a mixture of ethene dibromide, silver acetate, and glacial acetic acid in the water bath, and exhausting the digested mass with ether. On distilling the etheral solution, the ether first passes over, then the acetic acid, and lastly, when the temperature has reached $187^\circ C.$ ($368.6^\circ F.$), ethene diacetate. It is a colorless, neutral liquid, of sp. gr. 1.128 at 0° , boiling at $186^\circ C.$ ($366.8^\circ F.$), soluble in 7 parts of water and in every proportion in alcohol and ether. By distillation with potash it yields ethene alcohol, or glycol, $C_2H_4(HO)_2$.

PROPENYL OR GLYCERYL ACETATES; ACETINS.—These ethers are derived from propenyl alcohol (glycerin) by substitution of 1, 2, or 3 equivalents of acetyl for hydrogen. The formula of glycerin being $(C_3H_5)(OH)_3$, those of the three acetins are:

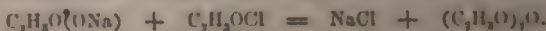
| | |
|--------------------|----------------------------|
| Monoacetin | $(C_3H_5)(OH)(OC_2H_3O)$ |
| Diacetin | $(C_3H_5)(OH)(OC_2H_3O)_2$ |
| Triacetin | $(C_3H_5)(OC_2H_3O)_3$ |

They are oily liquids, produced by heating glycerin and acetic acid together, in various proportions, in sealed tubes.

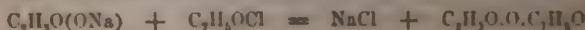
ACETIC CHLORIDE OR ACETYL CHLORIDE, C_2H_3OCl .—This compound, which has the constitution of acetic acid with chlorine substituted for hydroxyl, is produced, as already observed (p. 688), by the action of phosphorus trichloride, pentachloride, or oxychloride on glacial acetic acid. The product heated with water and dilute soda-solution, to remove phosphorus oxychloride and hydrochloric acid, and then rectified, yields acetyl chloride as a colorless liquid, having a suffocating odor, and emitting decomposes of hydrochloric acid in contact with the air. It has a density of 1.1305 at 0° , boils at $55^\circ C.$ ($131^\circ F.$), and is decomposed by water and alkaline solutions, yielding hydrochloric and acetic acids.

ACETIC OXIDE OR ANHYDRIDE, $C_2H_3O_2 = (C_2H_3O)_2O$, sometimes called *Anhydrous Acetic acid*.—This compound is obtained:

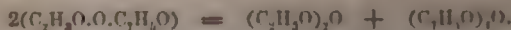
1. By the action of acetyl chloride on potassium or sodium acetate.



2. By heating sodium acetate with benzoyl chloride, C_7H_5OCl , whereby benzo-acetic oxide, $(C_2H_3O)(C_7H_5O)O$, is formed in the first instance, and subsequently resolved into acetic and benzoic oxides, the former distilling over, while the latter remains:



and:



Acetic oxide is a heavy oil which boils at $121^\circ C.$ ($249.8^\circ F.$), and dissolves slowly in water, being gradually converted into acetic acid:



Acetyl Peroxide, $(C_2H_3O)_2O_2$, obtained by adding barium dioxide to an etheral solution of acetyl monoxide, is a viscid liquid, which explodes with violence when heated, and acts as a powerful oxidizing agent.

Acids derived from Acetic Acid by Substitution.

Chloracetic Acids.—The three acids, C_2H_3ClO , $C_2H_2Cl_2O$, and C_2HCl_3O , are produced by the action of chlorine on acetic acid in sunshine; the second, however, is formed in small quantity only, the first or the third being produced in greatest abundance according as the acetic acid or the chlorine is in excess.

Monochloracetic acid. $CH_2Cl.COOH$, is produced, according to R. Hoffmann, by the action of chlorine on boiling glacial acetic acid in sunshine. Dr. H. Müller finds that the formation of monochloracetic acid is facilitated by dissolving a little iodine in the hydrated acetic acid, and passing a stream of chlorine through the boiling solution. On submitting the products of this reaction to repeated distillation, monochloracetic acid is obtained as a liquid, boiling at $185^\circ C.$ ($366.8^\circ F.$), and solidifying to a crystalline mass, which melts at $62^\circ C.$ ($143.6^\circ F.$), and dissolves easily in water. Heated with potash, it is converted into potassium glycollate, $KC_2H_3O_2$ (p. 689).

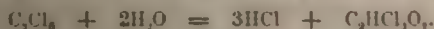


Dichloracetic acid, $CHCl_2.COOH$, is produced, together with the preceding compound, by the action of chlorine and iodine on boiling acetic acid, and is found in the portion of the product which boils above $188^\circ C.$ ($370.4^\circ F.$). According to Maumené, it may be obtained by exposing monochloracetic acid in flasks to the action of dry chlorine (5 atoms of chlorine to 3 molecules of chloracetic acid) for twenty-four hours, warming the product to expel hydrochloric acid and then distilling. It is a liquid having a specific gravity of 1.5216 at $15^\circ C.$ ($59^\circ F.$), and boiling at $190-191^\circ C.$ ($374-375.8^\circ F.$). According to Müller, it remains liquid when cooled; but according to Maumené, it crystallizes in rhombohedral plates. It forms a soluble silver salt, $AgC_2HCl_2O_2$, which is decomposed when its solution is heated with silver oxide to 75° or $80^\circ C.$ ($167-176^\circ F.$), giving off a mixture of carbon monoxide and dioxide:



Trichloracetic acid, $CCl_3.COOH$.—Discovered by Dumas. When a small quantity of crystallizable acetic acid is introduced into a bottle of dry chlorine gas, and the whole exposed to the direct solar rays for several hours, the interior of the vessel is found coated with a white crystalline substance, which is a mixture of trichloracetic acid with a small quantity of oxalic acid.

Trichloracetic acid may also be produced synthetically, viz., by the action of chlorine and water on carbon dichloride, C_2Cl_4 , this compound first taking up 2 atoms of chlorine and forming carbon trichloride, C_2Cl_6 , and the latter being converted by the water into hydrochloric and trichloracetic acids:



Trichloracetic acid is a colorless and extremely deliquescent substance: it has a faint odor, and sharp caustic taste, bleaching the tongue and destroying the skin; the solution is powerfully acid. It melts at $52^\circ C.$ ($125.6^\circ F.$), and boils without decomposition at $195-200^\circ C.$ ($383-392^\circ F.$) giving off a very irritating vapor. The density of the fused acid is 1.617.

Potassium trichloracetate, $2KC_2Cl_3O_2.Aq.$, crystallizes in fibrous silky needles, permanent in the air. The ammonium-salt, $2(NH_4)C_2Cl_3O_2 + 5Aq.$, is

or sodium amalgam is put into a strong aqueous solution of acid, the temperature of the liquid rises, without disengaging gas, and the solution is found to contain acetate and chloride of sodium, together with caustic alkali.

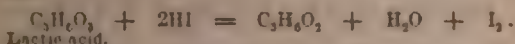
Bromacetic Acids.—The *mono-* and *di-*brominated acids are obtained by heating acetic acid or ethyl acetate with bromine in a retort at 180°C . (356°F). $\text{CH}_2\text{Br}.\text{CO}_2\text{H}$ crystallizes in deliquescent prisms, and boils at 208°C . (406.4°F). Its *ethylic ether* is a liquid, boiling at 159°C . (318.2°F). The acid is converted by ammonia into ammonium bromide. $\text{C}_2\text{H}_2\text{Br}_2.\text{CO}_2\text{H}$ is a crystalline mass melting at 45°C . (122°F), and boiling at 232°C – 234°C . (449.6° – 453.2°F). On treatment with moist silver oxide it yields bromo-glycolic acid, $\text{C}_2\text{H}_3\text{BrO}_3$, which boils at 192°C – 195°C . (377.6° – 383°F). *Tribromacetic acid*, $\text{C}_2\text{HBr}_3.\text{CO}_2\text{H}$, is produced by the action of water on tribromoacetyl chloride, $\text{C}_2\text{HBr}_3.\text{COCl}$, and by oxidation of bromal, $\text{CBr}_3.\text{COH}$, with nitric acid. It crystallizes in deliquescent crystals, melts at 130°C . (266°F), and boils at 473°F .

Iodacetic Acid, *mono-* and *di-*, are obtained by heating the corresponding brominated acids with potassium iodide; also by heating acetic acid with iodide and iodic acid. $\text{C}_2\text{H}_2\text{I}.\text{CO}_2\text{H}$ crystallizes in laminae, melting with partial decomposition at 82°C . (179.6°F). It is converted into acetic acid by boiling with HI . Its *ethylic ether* boils at 178°C – 180°C . (352.4° – 356°F).

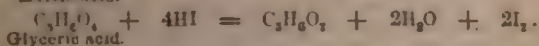
Cyanacetic Acid, $\text{C}_2\text{H}_3\text{NO}_2 = \text{CH}_2(\text{CN}).\text{CO}_2\text{H}$, is formed by heating monochloroacetic acid with potassium cyanide and water, in a retort, the mass melting at about 80°C . (176°F), and decomposed at 170°C into CO and acetonitril, $\text{CH}_3.\text{CN}$.

Thiaoacetic Acid, $\text{C}_2\text{H}_3\text{OS}$, or $\text{CH}_3.\text{COSH}$.—This acid, known to Kekulé, is formed by the action of phosphorus pentasulphide on acetic acid:

neous action of water and carbonyl chloride on ethane (p. 686). 4. By the oxidation of normal propyl alcohol (p. 589), and of propionic aldehyde, C_2H_5O . 5. Together with acetic acid, by oxidizing propione, $C_5H_{10}O$, with dilute chromic acid. This is the process by which it was first obtained. 6. From lactic acid and from glyceric acid by the action of hydriodic acid:



Lactic acid.



Glyceric acid.

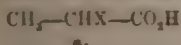
7. Together with several other products, in the fermentation of glycerin, and likewise of sugar, by the action of putrid cheese in presence of calcium carbonate.

Propionic acid is usually prepared by the second of the above-mentioned processes. Ethyl cyanide is added by drops to a moderately strong solution of potash heated in a tubulated retort, the distillate being repeatedly poured back as long as it smells of ethyl cyanide. The residue in the retort, consisting of potassium propionate, is then evaporated down to dryness, and distilled with syrupy phosphoric acid.

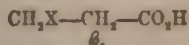
Propionic acid is a colorless liquid, having a specific gravity of 0.992 at 15°C . (64.4°F .), and boiling at 140°C . (284°F .). It is soluble in water, and when the water is quite saturated with it, the excess of acid floats on the surface in the form of an oil.

The propionates are soluble in water. The barium salt, $(\text{C}_3\text{H}_5\text{O}_2)_2\text{Ba} + \text{H}_2\text{O}$, crystallizes in rhombic prisms, and yields propione by dry distillation. The silver salt, $\text{C}_3\text{H}_5\text{O}_2\text{Ag}$, crystallizes in slender needles.

Substitution-products.—The replacement of one hydrogen-atom in propionic acid by a haloid element, X, yields two series of substitution-products distinguished as *a* and *b*; viz.:



a.



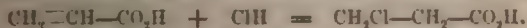
b.

Chloropropionic acids, $\text{C}_3\text{H}_5\text{ClO}_2$.—The *a*-acid is formed by decomposing lactyl chloride with water:



It is a thick liquid of specific gravity 1.28, and boiling at 186°C . (366.8°F .). When heated with moist silver oxide, it is converted into *a*-lactic acid, $\text{CH}_3\text{—CHOH—CO}_2\text{H}$. Its ethylic ether, obtained by heating lactyl chloride with alcohol, boils at 144°C . (291.2°F .).

The *b*-acid is produced by the action of chlorine-water on *b*-iodopropionic acid, and by addition of hydrogen chloride to acrylic acid, $\text{C}_3\text{H}_4\text{O}_2$:



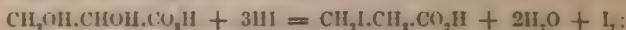
It is crystalline, and melts at 40.5°C . (104.9°F .). Its ethylic ether boils at about 155°C . (311°F .).

Bromopropionic acids, $\text{C}_3\text{H}_5\text{BrO}_2$.—The *a*-acid is obtained by the action of bromine on propionic acid, and by heating *a*-lactic acid (ordinary lactic acid) with hydrobromic acid, is a liquid which solidifies at -17°C . (1.4°F .), and boils at 202°C . (395.6°F .). Its ethylic ether smells like camphor, and boils at 190°C . (374°F .). Alcoholic ammonia converts it into *a*-amidopropionic acid or alanine, $\text{C}_3\text{H}_7(\text{NH}_2)\text{O}_2$ (see AMIDES). The *b* acid, formed by the action of bromine-water on *b*-iodopropionic acid, and

by addition of hydrobromic acid to acrylic acid, is crystalline, and melts at 61.5°C . (142.7°F .).

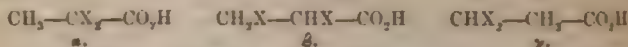
α -Iodopropionic acid, $\text{C}_3\text{H}_5\text{IO}_2$, is a thick oil, obtained by the action of phosphorus iodide on *α -lactic acid*.

The *β -acid* is obtained by the action of phosphorus iodide and a small quantity of water on glyceric acid:



also by addition of hydriodic acid to acrylic acid. It crystallizes in large colorless six-sided plates, having a peculiar odor, and melting at 82°C . (179.6°F .); easily soluble in hot water. By heating with strong hydriodic acid, it is reduced to propionic acid.

The di-substitution products of propionic acid admit of three modifications, viz.:



The first two modifications of the chlorine and bromine derivatives are known.

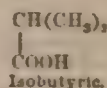
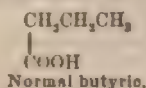
α -Dibromopropionic acid, $\text{CH}_3-\text{CBr}_2-\text{CO}_2\text{H}$, obtained by direct bromination of propionic or *α -bromopropionic acid*, melts at 61°C . (141.8°F .), and boils at 220°C . (428°F .). Its ethylic ether boils at 190°C . (374°F .).

β -Dibromopropionic acid, $\text{CH}_2\text{Br}-\text{CHBr}-\text{CO}_2\text{H}$, obtained by oxidation of dibromopropyl alcohol, $\text{C}_3\text{H}_6\text{Br}_2\text{O}$ (formed by addition of bromine to allyl alcohol), and by addition of Br_2 to acrylic acid, $\text{CH}_2=\text{CH}-\text{CO}_2\text{H}$, forms crystals easily soluble in water, melting at 65°C . (149°F .), decomposed by distillation. The ethylic ether boils at 212°C . (413.6°F .).

α -Dichloropropionic acid, $\text{CH}_3-\text{CCl}_2-\text{CO}_2\text{H}$. The ethylic ether of this acid is formed by the action of alcohol on the chloride, $\text{CH}_3-\text{CO}-\text{COCl}$, produced by the action of phosphorus pentachloride on pyracemic acid, $\text{CH}_3-\text{CO}-\text{COOH}$. It is a colorless liquid, having a pleasant odor of apples, a specific gravity of 1.2493 at 0° , and boiling at 160°C . (320°F .). Heated with water to 150°C . (302°F .), it is converted into pyracemic acid.

β -Dichloropropionic acid, $\text{CH}_2\text{Cl}-\text{CHCl}-\text{CO}_2\text{H}$, is formed by the action of water on the chloride obtained by heating glyceric acid with phosphorus pentachloride.

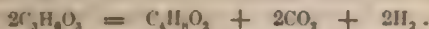
Butyric acid, $\text{C}_4\text{H}_8\text{O}_2 = \text{C}_3\text{H}_7.\text{CO}_2\text{H}$.—Of this acid there are two modifications, viz.:



Normal Butyric acid, also called *Fermentation Butyric*, *Propyl-formic*, and *Ethyl-acetic acid*, occurs, either free or combined with bases, in tamarinds and a few other plants, in certain beetles, in flesh-juice, in human perspiration, and in various kinds of decomposing vegetable and animal matter. As a glyceride, it occurs in various animal and vegetable fats, especially in the butter of cows' and goats' milk; as a hexyl ether in the oil of *Heracleum giganteum*, and as an octyl ether in oil of parsnip (*Pastinaca sativa*). It is formed by the oxidation of normal butyl alcohol, by the action of nascent hydrogen on crotonic acid, $\text{CH}_3-\text{CH}=\text{CH}-\text{CO}_2\text{H}$, by heating normal propyl cyanide (butyronitril) with alkalis or acids;

by the action of sodium and ethyl iodide on ethyl acetate (p. 687); and by the fermentation of sugar in contact with putrid cheese.

This last reaction affords the most convenient method of preparing the acid. The fermentation takes place, however, only in neutral liquids, so that it is necessary to add chalk, in order to neutralize the acid as fast as it is formed. The sugar is first converted into lactic and afterwards into butyric acid. The following proportions give a good result: 6 pounds of cane-sugar and half an ounce of tartaric acid are dissolved in 26 pounds of boiling water, and the solution is left for some time to allow the cane-sugar to pass into grape-sugar. To this solution about 4 ounces of decayed cheese diffused in 8 pounds of sour skim-milk, together with 3 pounds of chalk, are added, and the whole is kept for some weeks at a temperature of $30-35^{\circ}\text{C}$. ($86-95^{\circ}\text{F}$). The mixture is frequently stirred, and generally solidifies in ten or twelve days to a thick mass of calcium lactate. This, however, soon disappears, the mixture becoming liquid, and the lactate being converted into butyrate, with simultaneous evolution of carbon dioxide and hydrogen:—



When fermentation is completed, a solution of 8 pounds of crystallized sodium carbonate is added, and the filtered liquid, after concentration, is decomposed by sulphuric acid. Butyric acid then separates as an oily layer, which is dried over calcium chloride and rectified.

Butyric acid is a viscid liquid having a rancid odor, solidifying at -12°C . (10.4°F), and boiling at 163°C . (325.4°F). Specific gravity 0.958 at 14°C . (57.2°F). It dissolves easily in water and in alcohol, and separates from the aqueous solution on addition of salts.

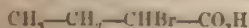
The metallic butyrates are, for the most part, soluble in water and crystallizable. The calcium salt, $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca} + \text{H}_2\text{O}$, forms shining laminae, and is more soluble in cold than in hot water. The silver salt, $\text{C}_4\text{H}_7\text{O}_2\text{Ag}$, crystallizes in shining laminae, soluble in 400 parts of water at 14°C . (57.2°F).

Ethyl Butyrate, $\text{C}_4\text{H}_7\text{O}_2.\text{C}_2\text{H}_5$, is a liquid having a pleasant fruity odor, and boiling at 119°C . (246.2°F).

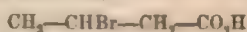
The butyrates unite with acetates, forming double salts, which react like salts of butyracetic acid, $\text{C}_4\text{H}_5\text{O}_2.\text{C}_2\text{H}_3\text{O}_2$, isomeric with propionic acid. This acid, obtained in the free state by the fermentation of calcium tartrate, differs from propionic acid in being resolved by distillation into butyric and acetic acids.

A *monochlorobutyric acid*, $\text{C}_4\text{H}_7\text{ClO}_2$, crystallizing in slender needles and melting at 99°C . (210°F), is formed by the action of chlorine on butyric acid in presence of iodine.

Out of five possible *monobromobutyric acids*, two, viz.,



α,



β,

are formed by the addition of HBr to crotonic acid. The action of bromine on butyric acid yields chiefly the α-acid, the ethylic ether of which boils at $170-172^{\circ}\text{C}$. ($338-341.6^{\circ}\text{F}$). The two acids are converted by boiling with potash-solution or moist silver oxide into the corresponding oxy-butyric acids, $\text{C}_4\text{H}_7\text{O}_3$.

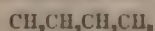
A *dibromobutyric acid*, $\text{C}_4\text{H}_6\text{Br}_2\text{O}_2$, melting at $45-48^{\circ}\text{C}$. ($113-118.4^{\circ}\text{F}$), is formed by further bromination of butyric acid.

Isobutyric Acid, $HC(CH_3)_2 \cdot CO_2H$, also called *Isopropyl-formic* and *(β -methyl-acetic acid*, occurs in the free state in St. John's bread, the fruit of *Ceratonia siliqua*, and as an acetylic ether in parsnip-root. It is produced by oxidation of isobutyl alcohol, by the action of alkalis or acids on isopropyl cyanide; and by the action of sodium and methyl iodide on ethyl acetate (p. 687).

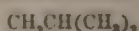
This acid is very much like normal butyric acid, but has a less disagreeable odor, and is not miscible with water. It has a specific gravity of 0.960 at 0° , and boils at $164^\circ C.$ ($309.2^\circ F.$). Its *calcium salt*, $(C_4H_7O_2)_2Ca + 5H_2O$, crystallizes in monoclinic prisms, much more soluble in hot water than in cold. The silver salt dissolves in 110 parts of water at $16^\circ C.$ ($60^\circ F.$). The *ethyl ether*, $C_4H_7O_2 \cdot C_2H_5$, has a specific gravity of 0.8893 at 0° , and boils at $110^\circ C.$ ($230^\circ F.$).

Bromoisobutyric acid, $(CH_3)_2CBr \cdot CO_2H$, formed by heating isobutyric acid with bromine to $140^\circ C.$ ($284^\circ F.$), forms crystals melting at $45^\circ C.$ ($113^\circ F.$), and is partly decomposed by boiling. Its ethylic ether has a specific gravity of 1.328 at 0° , and boils at 158° – $159^\circ C.$ (316.4° – $318.2^\circ F.$). By heating with moist silver oxide or baryta-water, this acid is converted into the corresponding oxyisobutyric acid.

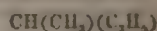
Pentolic or Valeric Acids, $C_5H_{10}O_2 = C_5H_9O(OH)$.—These acids admit of four metameric modifications, namely:—



Propyl acetic.



Isopropyl acetic.



Methyl-ethyl acetic.



Trimethyl acetic.

The first and second are obtained by oxidation of normal pentylic and isopentylic or amyl alcohol (p. 583) respectively; the third is not known, the fourth is produced from tertiary butylic alcohol or trimethyl-carbinol.

Propyl-acetic or Normal Valeric Acid, $C_5H_{11} \cdot COOH$, is an oily liquid, smelling like butyric acid, having a sp. gr. of 0.9577 at 0° , and boiling at $185^\circ C.$ ($365^\circ F.$).

Isopentolic, Isopropyl-acetic or Isovaleric Acid (ordinary valeric acid), occurs in valerian root, in angelica root, in the berries of the greater rose (*Viburnum Opulus*), and probably in many other plants. It is produced by the oxidation of ordinary amyl alcohol, either by absorption of atmospheric oxygen under the influence of platinum black, or by treatment with aqueous chromic acid, or by heating it with a mixture of caustic potash and quick-lime, the reaction, in this last case, being attended with evolution of hydrogen:



The potassium salt, distilled with sulphuric acid, yields the acid.

The most advantageous mode of preparing isovaleric acid, is to oxidize amyl alcohol with a mixture of sulphuric acid and potassium dichromate. 4 parts of the dichromate in powder, 6 parts of oil of vitriol, and 8 parts of water are mixed in a capacious retort, and 1 part of amyl alcohol is added by small portions, with strong agitation, the retort being plunged into cold water to moderate the violence of the reaction. When the change appears complete, the deep-green liquid is distilled nearly to dryness; the product mixed with excess of caustic potash, and the aqueous solution separated mechanically from a pungent, colorless, oily liquid which floats upon it, consisting of amyl valerate. The alkaline solution is then evaporated.

rated to a small bulk, and decomposed by dilute sulphuric acid in excess. The greater part of the valeric acid then separates as an oily liquid lighter than water: this is a hydrate consisting of $C_5H_{10}O_2.H_2O$. When distilled alone, it undergoes decomposition: water, with a little of the acid, first appears, and eventually the pure acid, $C_5H_{10}O_2$, in the form of a thin, mobile, colorless oil, having the persistent and characteristic odor of valerian root. It has a sharp and acid taste, reddens litmus strongly, bleaches the tongue, and burns when inflamed with a bright, yet smoky light. Isovaleric acid has a density of 0.947 at 0° , and boils at $175^\circ C.$ ($347^\circ F.$). Placed in contact with water, it absorbs a certain quantity, and is itself to a certain extent dissolved.

Isovaleric acid is active or inactive to polarized light, accordingly as it has been prepared from active or inactive amyl alcohol. That which has been prepared from the active alcohol produces a right-handed rotation of -3° in a tube 50 centimetres long. The difference between these two acids, like that of the alcohols from which they are derived, is probably due to difference rather of molecular than of atomic arrangement (p. 491).

The metallic isovalerates are greasy to the touch, and mostly crystallize with difficulty. Small fragments of them thrown on water, rotate on the surface as they dissolve. The barium salt $(C_5H_9O_2)_2Ba + H_2O$ usually crystallizes in thin laminae, soluble in two parts of cold, and in a smaller quantity of warm water. The zinc salt $(C_5H_9O_2)_2Zn$ forms shining scales. The silver salt $C_5H_9O_2Ag$ forms scales soluble in 540 parts of water at $20^\circ C.$ ($68^\circ F.$). A solution of potassium valerate, subjected to electrolysis, yields dibutyl, C_8H_{18} (p. 687).

Ethyl isovalerate, $C_5H_9O_2.C_2H_5$, is obtained by passing hydrochloric acid gas into an alcoholic solution of valeric acid. Ammonia converts it into valeramide, $C_5H_9ONH_2$. It is decomposed by sodium in the same manner as ethyl acetate (p. 687), yielding sodium ethylate and the sodium salt of an acid, $C_{13}H_{25}O_3$:



CHLOROVALERIC ACIDS.—Trichloroisovaleric acid, $C_5H_6Cl_3O_2$, obtained by the prolonged action of chlorine on isovaleric acid in the dark, aided towards the end of the process by a gentle heat, is an oily liquid, becoming very viscid at $18^\circ C.$ ($64.4^\circ F.$), perfectly mobile at $36^\circ C.$ ($86^\circ F.$). In contact with water it forms a very viscid hydrate, which sinks to the bottom. It dissolves in aqueous alkalis, and is precipitated by acids in its original state.

Tetrachloroisovaleric acid, $C_5H_4Cl_4O_2$, is the ultimate product of the action of chlorine on the preceding compound, aided by exposure to the sun. It is a semi-fluid, colorless oil, destitute of odor, of powerfully pungent taste, and heavier than water. It can neither be solidified by cold, nor distilled without decomposition. In contact with water, it forms a hydrate containing $C_5H_6Cl_4O_2.H_2O$, which is slightly soluble in water, easily soluble in alcohol and ether.

Neopentoic or Trimethyl-acetic Acid, $(CH_3)_3C.COOH$, is obtained from tertiary butyl iodide, $(CH_3)_3CI$, by converting this ether into the cyanide, and distilling the latter with potash; also by oxidation of pinacolin, $CH_3-(CO)-(C(CH_3)_2)_2$. It is a laminar crystalline mass, melting at $34-35^\circ C.$ ($93.2^\circ-95^\circ F.$), and boiling at $161^\circ C.$ ($321.8^\circ F.$). It smells like acetic acid, and dissolves in 40 parts of water at $20^\circ C.$ ($68^\circ F.$).

The barium salt, $(C_5H_9O_2)_2Ba + 5H_2O$, and the calcium salt, $(C_5H_9O_2)_2Ca + 4H_2O$, crystallize in needles or prisms.

The silver salt, $C_5H_9O_2Ag$, is obtained by precipitation in glittering span-

gles. The *ethyl ether*, $C_6H_{12}O_2.C_2H_5$, has a specific gravity of 0.8772 at 0° , and boils at 118.5° C. (245.3° F.).

Hexoic or Caproic acids, $C_6H_{12}O_2 = C_6H_{11}.CO_2H$.—There are eight possible forms of these acids, analogous to the eight pentyl alcohols, and five of them are known, viz.:

1. **Normal Caproic or Pentyl-formic acid**, $CH_3(CH_2)_4.CO_2H$.—This acid is formed synthetically by heating normal pentyl cyanide, $CH_3(CH_2)_4.CN$, with strong potash-solution. It is also produced, together with other acids of the fatty series, by the oxidation of albuminous substances, and of fatty acids of higher atomic weight. It occurs in the free state in perspiration, as an octylic ether, $C_8H_{16}O_2.C_8H_{17}$, in the volatile oil of camphor (p. 591), as a glyceride in the butter of cows' milk, and abundantly in cocoa-nut oil. From this oil it may be prepared by saponifying with strong soda-lye, and distilling the soap with dilute sulphuric acid. The distillate contains caproic and caprylic acids, and, when neutralized with baryta and evaporated, yields crystals of barium caprylate, and afterwards verucose crystals of the caproate, which, when decomposed by sulphuric acid, yields caproic acid.

Normal caproic acid is a clear mobile oil, having a somewhat sudoriferous and pungent odor, a specific gravity of 0.945 at 0° , 0.895 at 99° C. (210.2° F.), and boiling at 205° C. (401° F.). The barium salt, $(C_6H_{11}O_2)_2Ba + 3H_2O$, dissolves in 6–7 parts of water at 23° C. (73.4° F.). The *ethyl ether*, $C_6H_{11}O_2.C_2H_5$, has a fruity smell, and boils at 167° C. (332.6° F.).

2. **Isocaproic or Isopentyl-formic acid**, $CH(CH_3)_2.CH_2.CH_2.CO_2H$, prepared from isopentyl (amyl) cyanide, has a specific gravity of 0.931 at 0° , and boils at 199° – 200° C. (390.2° – 392° F.). Its odor resembles that of the normal acid, but is stronger and more disagreeable. The calcium salt, $(C_6H_{11}O_2)_2Ca + 3H_2O$, dissolves in 9 parts of water at 18° C. (64.4° F.). The *ethyl ether*, $C_6H_{11}O_2.C_2H_5$, has a specific gravity of 0.887 at 0° , and boils at 160.4° C. (320.7° F.).

3. **Methylisopropyl-acetic acid**, $CH(CH_3)_2 > CH.CO_2H$, prepared from the iodide of methyl-isopropyl carbinol (amylene hydrate, p. 586), through the medium of the cyanide, is an oil having a fruity smell. Its calcium salt crystallizes in scales, and is more soluble in cold than in hot water.

4. **Diethyl acetic acid**, $C_2H_5 > CH.CO_2H$, prepared by the action of sodium and ethyl iodide on methyl acetate (p. 686), is an oil sparingly soluble in water. Its *silver salt*, $C_6H_{11}O_2.Ag$, crystallizes in shining needles. The *ethyl ether*, $C_6H_{11}O_2.C_2H_5$, boils at 151° C. (303.8° F.).

Dimethyl-ethyl acetic acid, $\left\{ \begin{smallmatrix} (CH_3)_2 \\ C_2H_5 \end{smallmatrix} \right\} C.CO_2H$, formed from tertiary butyl iodide, $(CH_3)_3(C_2H_5)Cl$, through the medium of the cyanide, is a liquid which boils at 187° C. (368.6° F.), and solidifies in the crystalline form at 14° C. (57.2° F.). Its *barium salt*, $(C_6H_{11}O_2)_2Ba + 5H_2O$, crystallizes in large laminæ.

Heptoic acids, $C_7H_{14}O_2 = C_7H_{13}.CO_2H$. Of the 17 possible modifications of these acids, one only is accurately known, viz.:

Normal Heptoic or Enanthylic acid, $CH_3(CH_2)_5.CO_2H$, which is formed by the action of boiling potash on normal hexyl cyanide, $CH_3(CH_2)_5.CN$, by the oxidation of normal heptyl alcohol, and from enanthol or hept-

toic aldehyde, $C_7H_{14}O$, (p. 672), by oxidation in the air, or with nitric acid, or with chromic acid; also by oxidation of castor-oil with nitric acid.

Enanthic acid is a transparent colorless oil, having an unpleasant odor like that of codfish. It boils at $223^{\circ}C.$ ($433.4^{\circ}F.$). It is insoluble in water, but soluble in alcohol and ether. When heated with baryta, it gives off hexane, C_6H_{14} , the baryta abstracting carbon dioxide: $C_7H_{14}O_2 = CO_2 + C_6H_{14}$. The potassium-salt subjected to electrolysis yields dihexyl, $C_{12}H_{26}$. The calcium salt, $(C_7H_{13}O_2)_2.Ca + H_2O$, crystallizes in flattened needles, soluble in 100 parts of water at $5^{\circ}C.$ ($45.4^{\circ}F.$). The ethylic ether, $C_7H_{13}O_2.C_2H_5$, has a fruity odor, a specific gravity of 0.873 at $16^{\circ}C.$ ($60.8^{\circ}F.$), and boils at $188^{\circ}C.$ ($370.4^{\circ}F.$).

Another heptenoic acid has been obtained by the action of amyl iodide on ethylic succinate, $CH_3Na.CO_2C_2H_5$.

Caprylic Acid, $C_8H_{16}O_2 = C_8H_{15}.CO_2H$, occurs as a glyceride in the butter of cows' milk and in cocoa-nut oil; it is also found in several kinds of fusel-oil, partly free, partly as an ethylic or amyllic ether. It is best prepared by saponification of cocoa-nut oil; its barium-salt, being very sparingly soluble, is easily separated from the barium-salt of caproic acid formed at the same time.

Caprylic acid has a faint but unpleasant odor, especially when warmed.

It solidifies at $12^{\circ}C.$ ($53.6^{\circ}F.$), melts at $15^{\circ}C.$ ($59^{\circ}F.$), and boils at $230^{\circ}-238^{\circ}C.$ ($456.8^{\circ}-460.4^{\circ}F.$). When boiled with nitric acid, it is converted into nitrocaprylic acid, $C_8H_{15}(NO_2)O_2$.

Primary octyl alcohol, $C_8H_{18}O$, obtained from Heraeum oil (p. 591), yields by oxidation with chromic acid an acid, $C_8H_{16}O_2$, solidifying at $12^{\circ}C.$ ($53.6^{\circ}F.$), melting at $16-17^{\circ}C.$ ($60.8^{\circ}-62.6^{\circ}F.$), boiling at $234^{\circ}-238^{\circ}C.$ ($453.2^{\circ}-460.4^{\circ}F.$), and doubtless identical with the caprylic acid of natural fats: but the primary octyl alcohol obtained from the octane of American petroleum yields by oxidation an acid isomeric with the above, inasmuch as when floating on water it remains liquid at 0° .

As the primary octyl alcohol of Heraeum oil is an iso-alcohol (p. 591), it follows that the caprylic acid formed from it by oxidation, and therefore also that obtained from natural fats, must be an iso-acid, viz., iso-heptyl-formic acid, $\begin{matrix} H_3C \\ H_3C \end{matrix} > CH-(CH_2)_4-CO_2H$.

Pelargonic or Nonylic Acid, $C_9H_{18}O_2 = C_8H_{17}.CO_2H$, was first obtained from the leaves of the geranium (*Pelargonium roseum*), in which it exists ready formed. It may be procured in large quantity by the action of nitric acid upon the essential oil of rue (which contains nonyl-methyl ketone, $C_9H_{18}.CO.CH_3$); also, together with several other acids of the fatty series, by the action of boiling nitric acid on oleic acid. It is also formed synthetically by the action of boiling alcoholic potash on primary octyl cyanide, $C_8H_{17}.CN$, prepared from the octyl alcohol of Heraeum oil. It is a liquid having a slightly unpleasant odor, solidifying at $12^{\circ}-12.5^{\circ}C.$ ($53.6^{\circ}-54.5^{\circ}F.$), and boiling at $253^{\circ}-254^{\circ}C.$ ($487.4^{\circ}-489.2^{\circ}F.$).

Ethyl Pelargonate, $C_8H_{17}O_2.C_2H_5$, may be easily produced by dissolving the acid in strong alcohol, and passing a current of hydrochloric acid through the solution. It is a liquid of specific gravity 0.862, and boiling at $250^{\circ}C.$ ($482^{\circ}F.$). It has a powerful and most intoxicating vinous odor.

The aroma possessed by certain wines appears to be due to the presence of the ether of pelargonic acid, which, in this case, is probably generated during fermentation. When such wines, or the residues of their fermentation, are distilled on the large scale, an oily liquid passes over towards the close of the operation, which consists, in a great measure, of the crude

ether: it may be purified by agitation with solution of potassium carbonate, freed from water by a few fragments of calcium chloride, and redistilled. The pelargonic ether obtained by this process was originally described as *ananthic ether*, and the acid as *ananthic acid*.

Rutic or Capric Acid, $C_{10}H_{20}O_2$.—This acid exists as a glyceride in ordinary butter and in cocoa-nut oil; it occurs also in several kinds of fusel-oil, and is formed by the oxidation of oleic acid and of oil of rose. It may be obtained pure and in tolerable quantity from the liquid which remains in the distillation of the fusel-oil of the Scotch distilleries (p. 584), after the amyl alcohol has been distilled off at $132^\circ C.$ ($269.6^\circ F.$). This residue consists chiefly of amyl rutate, $C_{10}H_{18}O_2 \cdot C_5H_{11}$, and when distilled with potash gives off amyl alcohol and leaves potassium rutate, from which the rutic acid may be obtained by distillation with sulphuric acid.

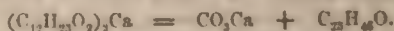
Rutic acid is a colorless crystalline body, having a slight odor of the goat, becoming stronger when the acid is warmed. It melts at $27-30^\circ C.$ ($80.6-86^\circ F.$), boils at $268-270^\circ C.$ ($514.4-518^\circ F.$), is very soluble in cold alcohol and ether, insoluble in cold water, slightly soluble in boiling water, and dissolves without alteration in strong nitric acid.

The metallic rutates are mostly sparingly soluble in water. The barium salt, $(C_{10}H_{19}O_2)_2Ba$, separates from solution in boiling water in needle-shaped or large prismatic crystals which float on the water if not moistened.

Lauric Acid, $C_{12}H_{24}O_2$, occurs as a glyceride (laurostearin) in the fat of the bay-tree (*Laurus nobilis*), and in the solid fat and volatile oil of pichurim beans (*Faba Pichurim maj.*). It is prepared by saponifying these fats with caustic alkali, and decomposing the resulting soap with tartare or hydrochloric acid. It likewise occurs, together with other fatty acids, or their glycerides, in cocoa-nut oil and the oils or fats of several other plants, also in spermaceti; and is separated from the mixtures of fatty acids resulting from the saponification of these substances by a complicated process of fractional precipitation with barium and magnesium salts, into the details of which we cannot enter.*

Lauric acid is insoluble in water, but dissolves easily in alcohol and ether, and crystallizes from alcohol in white, silky needles, which melt at about $43^\circ C.$ ($109.4^\circ F.$).

The laurates of the alkali-metals and of barium are soluble in water; the other salts are insoluble or sparingly soluble. The calcium salt, $(C_{12}H_{23}O_2)_2Ca$, is resolved by distillation into calcium carbonate and laurostearone:



Myristic Acid, $C_{14}H_{28}O_2$, occurs as a glyceride in nutmeg-butter and Otoba fat; also, together with lauric acid, in Dika bread, the fruit of *Mangifera gabonensis*, an African tree; and, together with other fatty acids, in cocoa-nut oil and spermaceti. It may be produced from crude ethal (cetyl alcohol) by heating with a mixture of potash and lime, its formation being doubtless due to the presence of methal or myristic alcohol, $C_{14}H_{28}O$, in the crude ethal (p. 594):



Lauric acid is likewise produced by a similar process from crude ethal, doubtless because that substance also contains lethal or lauric alcohol, $C_{12}H_{26}O$.

Pure myristic acid is most easily obtained by saponification of Otoba fat

* See Watts's Dictionary of Chemistry, vol. III. p. 474.

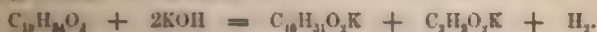
(from *Myristica Oboea*). It forms white, shining crystalline laminae, melting at 53.8°C . (128.8°F). It is quite insoluble in water and in ether, but dissolves easily in hot alcohol, and crystallizes therefrom on cooling.

The myristates of the alkali-metals, $\text{C}_{14}\text{H}_{27}\text{O}_2\text{K}$, etc., are soluble in water, and not decomposed thereby (like the stearates). The other myristates are insoluble or sparingly soluble, and are obtained by precipitation.

Myristan (C_3H_5)($\text{C}_{14}\text{H}_{27}\text{O}_2$)₃, the glyceride of myristic acid, is obtained by pressing nutmegs between hot plates, exhausting the crude fat thus obtained with spirits of wine, and crystallizing the undissolved portion from boiling ether. It is a crystalline fat having a silky lustre.

Palmitic Acid, $\text{C}_{16}\text{H}_{32}\text{O}_2$, occurs as a glyceride (tripalmitin) in many natural fats, often associated with stearin. Palm-oil, the produce of *Elais guineensis*, Chinese tallow, the produce of the tallow-tree (*Stillingia sebifera*), and Japan wax, from *Rhus succedanea*, consists mainly of tripalmitin. Palmitic acid is easily prepared by saponifying palm-oil with caustic potash, decomposing the soap with sulphuric acid, and crystallizing the separated fatty acid several times from hot alcohol till it exhibits a constant melting-point. Chinese tallow may be saponified with alcoholic potash, and Japan wax by fusion with solid potassium hydrate, and the soap treated in a similar manner.

Palmitic acid exists also as cetyl palmitate (cetin), $\text{C}_{16}\text{H}_{33}\cdot\text{C}_{18}\text{H}_{37}\text{O}_2$, in spermaceti, and as myricyl palmitate (melissin), $\text{C}_{20}\text{H}_{41}\cdot\text{C}_{16}\text{H}_{31}\text{O}_2$, in bees'-wax. It is produced, together with acetic acid, by melting oleic acid, $\text{C}_{18}\text{H}_{34}\text{O}_2$, with potassium hydrate:



Palmitic acid is a colorless, solid body, without taste or smell, lighter than water. It is insoluble in water, but dissolves abundantly in boiling alcohol or ether. The solutions are acid, and when concentrated, solidify in a mass on cooling. When dilute they yield the acid in tufts of slender needles. It melts at 62°C . (143.6°F), and solidifies on cooling in a mass of shining mucous laminae. When heated in a dish it boils and evaporates without residue, and may be distilled almost without change. When gently heated in the air, it is but slightly altered, but at higher temperatures it takes fire, and burns with a bright smoky flame like other fats. It is attacked by chlorine at 100° , giving off hydrochloric acid, and forming oily substitution-products. Heated with alcohols, it forms compound ethers.

Palmitic acid forms normal or neutral salts, having the composition $\text{M}\text{C}_{16}\text{H}_{31}\text{O}_2$ for univalent, and $\text{M}''(\text{C}_{16}\text{H}_{31}\text{O}_2)_2$ for bivalent metals, and with the alkali-metals also, acid salts analogous to the acid acetates. The normal palmitates of potassium and sodium are soluble in water and alcohol; the rest are insoluble, and are obtained by precipitating a metallic salt with an alcoholic solution of sodium or potassium palmitate.

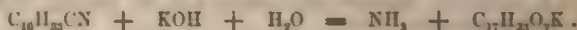
Ethyl palmitate, $\text{C}_2\text{H}_5\cdot\text{C}_{16}\text{H}_{31}\text{O}_2$, obtained by passing hydrochloric acid gas into a saturated alcoholic solution of palmitic acid, crystallizes in prisms, and melts at 24°C . (75.2°F).

Glyceryl Palmitates or Palmitins.—There are three of these ethers—viz., *Monopalmitin*, $\text{C}_3\text{H}_5\cdot\left\{(\text{OH})_2\cdot\text{C}_{16}\text{H}_{31}\text{O}_2\right\}$, *dipalmitin*, $\text{C}_3\text{H}_5\cdot\left\{\text{OH}\cdot\left(\text{C}_{16}\text{H}_{31}\text{O}_2\right)_2\right\}$, and *tripalmitin*, $\text{C}_3\text{H}_5\cdot(\text{C}_{16}\text{H}_{31}\text{O}_2)_3$. The first and second are obtained by heating palmitic acid with glycerin in sealed tubes; the third by heating a mixture of 1 part of monopalmitin and 10 parts of palmitic acid to 250°C . (482°F) for twenty-eight hours. They are all crystalline fats. Tripalmitin thus obtained melts at 46°C . (114.8°F). Natural palmitin,

obtained from palm-oil and other fats, has the composition of tripalmitin, but exhibits three isomeric (or rather allotropic) modifications (like those of stearin) melting respectively at 46°C . (114.8°F .), 61.7°C . (143.1°F .), and 62.8°C . (145°F .): the first appears to be identical with artificial tripalmitin.

Palm-oil comes chiefly from the coast of Africa. It has, when fresh, a deep orange-red tint and a very agreeable odor: the coloring matter—the nature of which is unknown—is easily destroyed by exposure to light, especially at a high temperature, and also by oxidizing agents. The oil melts at 27°C . (80.6°F .). By cautious pressure it may be separated into fluid olein and solid palmitin, which, when purified by crystallization from hot ether, is perfectly white. By keeping, palm-oil seems to suffer a change similar to that produced by saponification: in this state it is found to contain traces of glycerin and a considerable quantity of oleic acid, together with palmitic acid. The oil becomes harder and rancid, and its melting point is raised at the same time.

Margaric Acid, $C_{17}H_{34}O_2$.—This name was formerly applied to an acid, intermediate between stearic and palmitic acids, supposed to be produced, together with others, by the saponification of natural fats, but it is now restricted, for reasons to be presently mentioned, to an acid prepared by a definite reaction—viz., by the action of boiling alcoholic potash on cetyl cyanide:—



The solid potassium salt thus obtained is decomposed by boiling dilute hydrochloric acid, and the separated margaric acid is purified by precipitating its ammoniacal solution with barium chloride, decomposing the precipitate with hydrochloric acid and ether, separating the ethereal solution by means of a pipette; and distilling off the ether. It forms white crystals, melting at 59.9°C . (139.8°F .), and is intermediate in all its properties between palmitic and stearic acids.

The so-called margaric acid, obtained by the saponification of natural fats, and regarded by Chevreul* and many other chemists, as a distinct acid having the composition $C_{17}H_{34}O_2$, has been shown by Heintz† to be a mixture, resolvable into stearic acid and other fatty acids of lower melting point, chiefly palmitic acid. Such mixtures of solid fatty acids, or of the corresponding glycerides, cannot be completely resolved into their constituent fats by crystallization from alcohol, ether, or other solvents, which was the method of separation resorted to in the earlier investigations. The only effectual method of separation is to subject the alcoholic solution of the acids to a series of fractional precipitations with acetate of lead, barium, or magnesium, the stearate then separating out first.

Stearic Acid, $C_{18}H_{36}O_2$, was discovered by Chevreul as a constituent of the more solid fats of the animal kingdom. It is most abundant in these, especially in beef- and mutton-suet; but exists also, together with palmitic, myristic acid, etc., in the softer fats, such as the butter of cows-milk, human fat, that of the goose, of serpents, of cantharides, and in spermaceti. It occurs also in vegetable fats, especially those of cascade-beans, of the berries of *Cocculus indicus*, and in shea-butter, obtained from the nuts of *Bassia Parkii*, a tree growing in West Africa. In all these fats it occurs as a glyceride, but in that of cocculus grains also in the free state.

* *Recherches sur les corps gras d'origine animale.* Paris, 1823.

† For references to Heintz's memoirs, see Gmelin's Handbook, vol. xv. p. 343.

Stearic acid is prepared from beef or mutton-suet, or better, from cacao-fat, by saponifying the fat with soda-lye, heating the soap-paste with water and dilute sulphuric acid, removing the separated fatty acids after cooling, washing them with water, and then dissolving them in as small a quantity as possible of hot alcohol. On cooling, the greater part of the solid acid separates out, while the oleic acid remains in solution, and may be separated by subjecting the mass, after draining, to strong pressure, redissolving the residue in a small quantity of alcohol, leaving it to separate by cooling, and again pressing the solid mass. From the mixture of solid fatty acids thus obtained, the stearic acid may be separated in a comparatively pure state, by repeated crystallization from considerable quantities of alcohol, only the portion which first separates being each time collected. But to obtain pure stearic acid, it is better to dissolve the impure stearic acid (4 parts), melting at 60°C . (140°F .), in such a quantity of hot alcohol that nothing will separate out on cooling, even to 0° , and mix the hot liquid with a boiling alcoholic solution of magnesium acetate (1 part). The magnesium-salt which separates on cooling is pressed and boiled for some time with a large quantity of dilute hydrochloric acid, and the stearic acid thereby separated is repeatedly crystallized from alcohol, till it melts constantly at 69° to 70°C . (156.2° to 158.6°F .).

Stearic acid is also easily prepared from the fat of cocculus-berries, which consists mainly of stearin, by saponifying it with potash, etc. According to Buff and Oudemans, the best material for the preparation of stearic acid is shea-butter, which contains about 30 per cent. oleic acid, and 70 per cent. stearic, but no other solid fatty acid.

On the large scale, impure stearic acid is prepared for the manufacture of stearin-candles, by saponifying some of the harder fats, generally with lime. The resulting lime-soap, decomposed by sulphuric acid, yields a mixture of fatty acids, which are pressed, first in the cold, and afterwards at a higher temperature, in order to separate the oleic acid from the less fusible palmitic and stearic acids. Another method, applied chiefly to palm-oil, consists in decomposing the fat with super-heated steam, as described under GLYCERIN (p. 610). A third method consists in treating the fat with sulphuric acid, and distilling the product.

Pure stearic acid crystallizes from alcohol in nacreous laminae or needles; it is tasteless and inodorous, and has a distinct acid reaction. At low temperatures it is heavier than water, having a specific gravity of 1.01 at 0° ; but between 9° and 10°C . (48.2° – 50°F .) its specific gravity is the same as that of water. It melts at 69° – 69.2°C . (156.2° – 156.6°F .) to a colorless oil, which on cooling solidifies to a white, fine, scaly, crystalline mass, lamino-crystalline on the fractured surface. When heated, it distils, for the most part, without alteration. Chlorine converts it into chlorostearic acid, $\text{C}_{18}\text{H}_{33}\text{ClO}_2$. Heated with bromine and water in a sealed tube, it is converted into bromostearic acid, $\text{C}_{18}\text{H}_{33}\text{BrO}_2$, and dibromostearic acid, $\text{C}_{18}\text{H}_{34}\text{Br}_2\text{O}_2$.

Stearates.—Stearic acid dissolves in a cold aqueous solution of alkaline carbonate, probably from formation of acid carbonate, and does not expel the carbonic acid and form a mono-acid salt, till heated to about 100° . On the other hand, the stearates are decomposed by most other acids, the separated stearic acid rising to the surface as an oil when the liquid is warm. The stearates have the consistence of hard soaps and plasters, and are mostly insoluble in water. The normal potassium-salt, $\text{C}_{18}\text{H}_{35}\text{O}_2\text{K}$, separates on cooling from a solution of 1 part stearic acid and 1 part potassium hydrate in 10 parts of water, in white opaque granules. The acid salt, $\text{C}_{18}\text{H}_{35}\text{O}_2\text{K} \cdot \text{C}_{18}\text{H}_{35}\text{O}_2$, is obtained by decomposing the normal salt with 1000 parts or more of water, and separates in silvery scales from

on addition of common salt, in hard, unctuous masses, which in common use: this mode of separation is called *salting out* soaps, on the other hand, cannot be thus separated; for, on their solution, they are decomposed and converted into a form they are obtained in a semi-solid state by evaporating the products, called soft soaps, always contain a considerable alkali, and are used for cleansing and scouring when a power is required.

Stearic ethers are formed by heating stearic acid monatomic or polyatomic. *Ethyl stearate*, $C_2H_5.C_{18}H_{35}O_2$, is obtained by passing hydrochloric acid gas into an alcoholic solution of stearic acid. It resembles white wax, is inodorous and tasteless, (86° F.), and cannot be distilled without decomposition. It is decomposed by boiling with caustic alkalies. There are the stearates or stearins, analogous in composition to

Monostearin, $C_8H_7 \left\{ \begin{matrix} (OH)_3 \\ C_{18}H_{35}O_2 \end{matrix} \right\}$, prepared by heating a mixture of stearic acid and glycerin to 200° in a sealed tube for 36 hours; small white needles, melting at 61° C. (141.8° F.), and solid at 60° C. (140° F.).—*Distearin*, $C_8H_7 \left\{ \begin{matrix} OH \\ C_{18}H_{35}O_2 \end{matrix} \right\}_2$, obtained by heating stearic acid to 260° for three hours; microscopic laminae, melts at 58° C. (136.4° F.), and solid at 131° F.).—*Tristearin*, $C_8H_7(C_{18}H_{35}O_2)_3$, is prepared by heating with 15 to 20 times its weight of stearic acid to 270° C. (516° F.) in a sealed tube; also from various solid natural fats in ether, and repeated crystallization from the hot solution. It is obtained in masses of white pearly laminae or needles, inodorous, and volatilizing without decomposition under reduced pressure. Natural and artificial tristearin exhibit three isomeric or allotropic forms. Stearin separated from ether melts at 69.7° C. (157.5° F.), and when cooled to 73.7° C. (164.6° F.) or higher and then cooled, it does not solidify; cooled to 51.7° C. (125° F.). It then melts at 52° C. (125° F.) heated a few degrees higher, passes into a third modification.

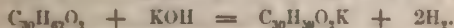
Benic or Behenic Acid, $C_{22}H_{44}O_2$, is obtained, together with other acids, by saponification of oil of ben, the oil expressed from the fruits of *Moringa Nuc Lichen*. It is a white crystalline fat, melting at $70^\circ C.$ ($168.5^\circ F.$), and solidifying at $70^\circ C.$ ($158^\circ F.$).

Cerotic Acid, $C_{27}H_{54}O_2$, is the essential constituent of *cerin*, the portion of bees'-wax which is soluble in boiling alcohol. It is prepared by heating the wax several times in succession with boiling alcohol, till the deposit which forms on cooling melts at 70° or $72^\circ C.$ (158° – $161.6^\circ F.$), and may be further purified by precipitating it from the boiling alcoholic solution with lead acetate, decomposing the precipitate with strong acetic acid, and crystallizing the separated acid from boiling alcohol. Cerotic acid is also produced by the dry distillation of Chinese wax, which consists of ceryl cerotate, $C_{37}H_{74}O_2 \cdot C_{27}H_{54}O_2$, or by melting that substance with potassium, and decomposing the resulting potassium-salt with an acid (p. 594).

Pure cerotic acid crystallizes in small grains, melting at $78^\circ C.$ ($172.4^\circ F.$), and distilling without alteration. Chlorine converts it into chlorocerotic acid, $C_{27}H_{43}ClO_2$, a thick transparent gum of a pale yellow color.

Ceryl cerotate, or *Chinese wax*, is produced on certain trees in China by the puncture of a species of *coccus*. It is crystalline, of a dazzling whiteness, like spermaceti, melts at $82^\circ C.$ ($179.6^\circ F.$); dissolves in alcohol; yields cerotic acid and cerylene, $C_{37}H_{74}$, by dry distillation. It is used in China for making candles.

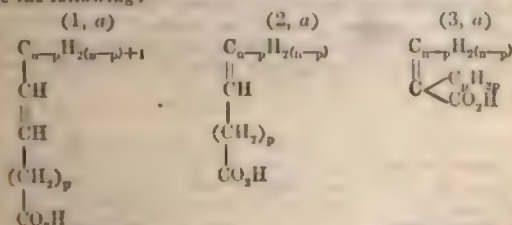
Melissic Acid, $C_{30}H_{60}O_2$, the highest known member of the fatty series, is obtained by heating myricyl alcohol (p. 595) with potash-lime:



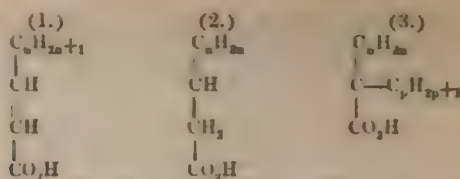
It bears considerable resemblance to cerotic acid, but melts at a higher temperature, viz., at 88° or $89^\circ C.$ (190.4° – $192.2^\circ F.$). The *silver-salt*, $C_{30}H_{57}O_2Ag$, is a white precipitate.

Monatomic Acids, $C_nH_{2n-2}O_2$.—Acrylic Series.

This series comprises three isomeric groups of acids, which may be represented by the following general formulæ, in which n and p denote any whole numbers from 0 upwards:*



The first of these formulæ is reducible to $C_n + 3H_{2n+4}O_2$ or $C_n + 3H_6(y+1)O_2$, and the second and third to $C_n + 2H_{2n+2}O_2$ or $C_n + 2H_4(y+1)O_2$, both of which are included under the general formula of the series $C_nH_{2n-2}O_2$. In all the known acids of the first group, however, except perhaps angelic acid, the value of $p = 0$, and in the only known acid of the second group, viz., isocrotonic acid, $p = 1$, so that for these known acids the two formulæ are reduced to the simpler forms given in the text.

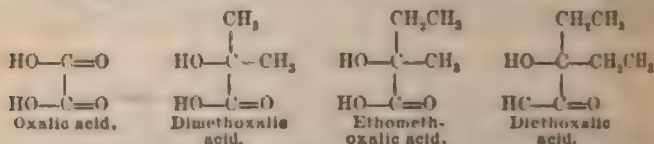


• Of the acids of the first group, called **normal acrylic acids**, some occur, mostly as glycerides, in vegetable and animal organisms, others are formed artificially by special processes. Most of them are only liquids. The known acids of this group are:

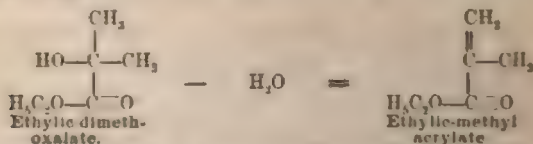
| | | | | | |
|------------------|---------|-------------------|-----------------|---------|-------------------|
| Acrylic acid | . . . | $C_3H_4O_2$ | Phytsoleic acid | } . . . | $C_{18}H_{30}O_2$ |
| Crotonic acid | . . . | $C_4H_6O_2$ | Hypogaeic acid | | |
| Angelie acid | . . . | $C_6H_8O_2$ | Gadlic acid | | |
| Pyroterebic acid | . . . | $C_8H_{10}O_2$ | Oleic acid | } . . . | $C_{18}H_{34}O_2$ |
| ? Damaluric acid | . . . | $C_7H_{12}O_2$ | Elaidic acid | | |
| ? Damolic acid | . . . | $C_{13}H_{24}O_2$ | Doeglic acid | . . . | $C_{18}H_{34}O_2$ |
| Moringic acid | } . . . | $C_{15}H_{28}O_2$ | Brassic acid | } . . . | $C_{22}H_{42}O_2$ |
| Cimicic acid | | | Brucic acid | | |

Of the acids of the second group only one is at present known, viz., **isocrotonic acid**, $C_4H_6O_2 = CH_2 = CH-CH_2-CO_2H$ [$n=1$].

The acrylic acids of the third group are formed by a general synthetical process, viz., by abstraction of the elements of water from certain acid ethers or alcoholic acids, having the composition of oxalic acid, $C_2H_2O_4$, in which 1 atom of oxygen is replaced by 2 atoms of a monatomic alcohol-radicle, C_nH_{2n+1} ; thus:



Now, when the ethylic ethers of these acids are treated with phosphoric oxide or phosphorus trichloride, they give up a molecule of water (H_2O), at the expense of one of the molecules of hydroxyl (OH) and of an atom of hydrogen abstracted from one of the monad alcohol-radicles, which is thereby converted into a dyad radicle (an olefine) capable of saturating the unit of equivalence of the carbon-atom set free by abstraction of the hydroxyl. The product is the ethylic ether of an acrylic acid of the third group; thus:—



The ethylic ether thus formed is converted into methacrylic acid by saponification with potash in the usual way. In this manner the following acids have been obtained:—

Methacrylic acid, $\text{CH}_2=\text{C} \begin{smallmatrix} \text{CH}_3 \\ \text{COOH} \end{smallmatrix}$, isomeric with Crotonic acid.

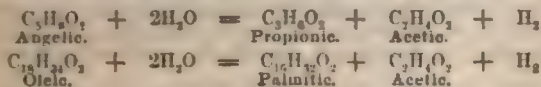
Methylcrotonic acid, $\text{C}_4\text{H}_6=\text{C} \begin{smallmatrix} \text{CH}_3 \\ \text{COOH} \end{smallmatrix}$, isomeric with Angelic acid.

Ethylcrotonic acid, $\text{C}_5\text{H}_8=\text{C} \begin{smallmatrix} \text{CH}_2\text{CH}_3 \\ \text{COOH} \end{smallmatrix}$, isomeric with Pyrotartaric acid.

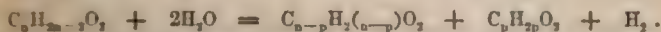
There might, of course, be an ethacrylic acid isomeric with methylcrotonic acid, and a propyl-acrylic acid isomeric with ethylcrotonic acid, but these have not yet been obtained.

The individual acids of the three groups differ from one another according to the values of n and p , and those which contain the radicle C_3H_5 , and its higher homologues, are susceptible of further modifications according to the structure of these radicles.

The acids of all three series, when fused with potash, are resolved, with evolution of hydrogen, into two acids of the fatty series:—



generally:



The manner in which this splitting up of the molecule takes place differs, however, according to the group to which the acid belongs. In the decomposition of an acrylic acid of the first group, one of the products is always acetic acid; in the second, one of the products is always propionic acid; while in the third, the two products may be any members of the fatty series of acids.

The final result of the action above mentioned is, in fact, to add 2 atoms of hydrogen and 2 atoms of oxygen to the molecule $\text{C}_n\text{H}_{2n-1}\text{O}_2$. Now, if

an acid of the first group, represented by the formula,

$\text{C}_n\text{H}_{2n-1}-\text{CH} \begin{smallmatrix} \vdots \\ \vdots \end{smallmatrix} \text{CH}-\text{CO}_2\text{H}$, we suppose H_2 to be added to the right of the dotted line, we get $\text{CH}_3-\text{CO}_2\text{H}$, which is the formula of acetic acid, while

the addition of O_2 to the left of the dotted line gives $\text{C}_n\text{H}_{2n+1}-\text{CO}_2\text{H}$, which is also the formula of a fatty acid. Similarly the addition of H_2 on the

right of the formula of the second group, $\text{C}_n\text{H}_{2n} \begin{smallmatrix} \vdots \\ \vdots \end{smallmatrix} \text{CH}-\text{CH}_2-\text{CO}_2\text{H}$, gives

$\text{CH}_3-\text{CH}_2-\text{CO}_2\text{H}$, which is the formula of propionic acid, while the addition of O_2 on the left gives $\text{C}_n\text{H}_{2n+2}\text{O}_2$, which represents another fatty acid.

The acrylic acids are also converted into fatty acids by the action of nascent hydrogen, e.g., crotonic acid, $\text{C}_4\text{H}_7\text{O}_2$, into butyric acid, $\text{C}_4\text{H}_9\text{O}_2$.

Acrylic Acid, $\text{C}_3\text{H}_3\text{O}_2 = \text{CH}_2=\text{CH}-\text{CO}_2\text{H}$ [$n = 0$ in formula 1].—This acid is the lowest possible member of the series, and does not admit of isomeric modifications. It is produced—(1) By oxidizing its aldehyde (acrolein), $\text{C}_3\text{H}_3\text{O}$, with moist silver oxide; (2) From α or β iodopropionic acid, $\text{CH}_3\text{CHI}.\text{CO}_2\text{H}$, or $\text{CH}_2\text{I}.\text{CH}_2.\text{CO}_2\text{H}$, by heating alone, or with alcoholic potash, whereby HI is abstracted; (3) By the action of nascent hydrogen (zinc and sulphuric acid) on β -dibromopropionic acid:—



Acrylic acid is a colorless liquid, having a pungent, slightly aromatic

odor, and miscible in all proportions with water. It solidifies at low temperatures, melts at $7^\circ C.$ ($44.6^\circ F.$), and boils at $139^\circ-140^\circ C.$ ($282.2-284^\circ F.$). Nascent hydrogen converts it into propionic acid. It unites with bromine, forming β -dibromopropionic acid, and with the haloid acids to form the β -substitution products of propionic acid. By fusion with potash it is resolved into formic and acetic acids.

The metallic acrylates, excepting the silver salt, are very soluble in water; they decompose at 100° . The silver salt, $C_3H_3O_2Ag$, and the lead salt, $(C_3H_3O_2)_2Pb$, crystallize in shining needles.

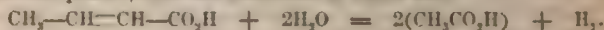
Ethyl Acrylate, $CH_2=CH-CO_2C_2H_5$, prepared from the ethylic ether of β -dibromopropionic acid by the action of zinc and sulphuric acid, is a pungent-smelling liquid, having a specific gravity of 0.925 at 0° , and boiling at $102^\circ C.$ ($215.6^\circ F.$).

Chloracrylic Acid, $C_3H_3ClO_2$, prepared by treating dichloropropionic acid with baryta-water, crystallizes in slender needles, which melt at $65^\circ C.$ ($149^\circ F.$).—*Bromacrylic Acid*, $C_3H_3BrO_2$. Of this acid there are two modifications, $CH_2=CHBr-CO_2H$ and $CHBr-CH=CO_2H$, obtained respectively from α - and β -dibromopropionic acid. The former melts at $70^\circ C.$ ($158^\circ F.$), and unites with hydrobromic acid, reproducing α -dibromopropionic acid.

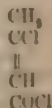
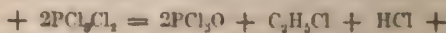
Crotonic Acids, $C_4H_6O_2=C_3H_5-CO_2H$.—Of these acids there are three modifications, viz.:

(1) **Solid Crotonic Acid**, $CH_3-CH=CH-CO_2H$.—This acid is formed— α . By oxidation of its aldehyde, $CH_3-CH=CH-CHO$ (p. 673); β . By the dry distillation of β -oxybutyric acid, $CH_3-CH(OH)-CH_2-COO_2H$ (abstraction of OHH); γ . By the action of alcoholic potash on α -bromobutyric acid, $CH_3-CH_2-CHBr-CO_2H$; δ . From allyl iodide by conversion into the cyanide, and distillation of the latter with potash. Now allyl iodide has the structure $CH_2=CH-CH_2I$ (p. 596), and therefore the cyanide might be expected to be $CH_2=CH-CH_2CN$, and the acid obtained from it, $CH_2=CH-COO_2H$, which is the structure of isocrotonic acid. But as the acid obtained in this manner is identical in its properties with that which is produced by the first three reactions, it must be inferred that, either in the conversion of the allyl iodide into cyanide, or of the latter into the acid, a transposition of atoms has taken place within the molecule.

Solid crotonic acid crystallizes in slender woolly needles, or in large plates, melts at $72^\circ C.$ ($161.6^\circ F.$), boils at $182^\circ C.$ ($359.6^\circ F.$), and dissolves in 12 parts of water at 20° . Nascent hydrogen converts it into normal butyric acid. It unites with hydrogen bromide, forming monobromobutyric acid, and with bromine to form dibromobutyric acid. By oxidation with nitric acid, it is resolved into acetic and oxalic acids, and by fusion with potash, into two molecules of acetic acid:



Monochlorocrotonic Acid, $C_4H_5ClO_2$, is produced by the action of zinc and hydrochloric acid on trichlorocrotonic acid; also by that of phosphorus pentachloride, and subsequently of water, on ethylic aceto-acetate, $(CH_3CO-CH_2-COOC_2H_5)$, whence it appears to have the structure $CH_3-CCl=CH-CO_2H$:



and



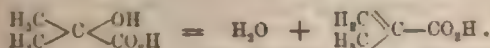
This acid dissolves in 35 parts of water at 19° C. (66.2° F.), melts at 2° C. (35.2° F.), and boils at 206°–210° C. (402.8°–410° F.). Sodium amalgam converts it into crotonic acid.

Trichlorocrotonic Acid, $C_4H_3Cl_3O_2$, produced by oxidation of the corresponding aldehyde with cold strong nitric acid, melts at 44° C. (111.2° F.).

(2) **Isocrotonic Acid**, $CH_2=CH-CH_2-CO_2H$ (Geuther's *quartenylic* acid), formed from its chloro-derivative (*infra*) by the action of sodium amalgam, is a non-solidifying liquid, having a specific gravity of 1.018 at 1° C. (77° F.), and boiling at 172° C. (341.6° F.). When heated in a red tube to 170°–180° C. (338°–356° F.), it is converted into solid crotonic acid. When fused with potash, it is resolved, not, as might be expected, into propionic and formic acids, but, in consequence of the transformation by heat just mentioned, into two molecules of acetic acid.

Chloroisocrotonic acid, $CH_2=CCl-CH_2-CO_2H$, is produced, together with crotonic acid, by the action of phosphorus pentachloride and water on ethylic aceto-acetate. It forms crystals slightly soluble in water, subliming at ordinary temperatures, melts at 59.5° C. (139.1° F.), and boils 105° C. (383° F.).

(3) **Methacrylic Acid**, $CH_2=C<\begin{smallmatrix} CH_3 \\ CO_2H \end{smallmatrix}$ [$n=1$, $p=1$ in formula 3, p. 6], is formed by the action of phosphoric oxide or phosphorus trichloride on ethylic dimethoxalate (p. 714), and by that of phosphorus trichloride on oxyisobutyric acids:



It is a liquid which does not solidify at 0°. By fusion with potash it is resolved into formic and propionic acids.

Five-carbon Acrylic Acids, $C_5H_8O_2 = C_4H_7.CO_2H$.—Of these acids, two only are known, namely, angelic and methyl-crotonic acid.

Angelic Acid exists in the root of the archangel (*Angelica Archangelica*), and in sumbul or moschus root, a drug imported from Asia Minor, and probably also belonging to an umbelliferous plant. It is obtained from archangel root, by boiling the root with lime and water, and distilling the strained and concentrated liquid with dilute sulphuric acid. It is also produced by heating the essential oil of chamomile, which consists of angelic aldehyde together with a hydro-carbon, with potassium hydroxide:



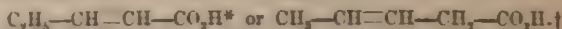
So, together with oroselin, by treating pencedanin or imperatorin (a neutral substance contained in the root of *Imperatoria Ostruthium*, and some other umbelliferous plants) with alcoholic potash:



Angelic acid crystallizes in long prisms and needles, melts at 45° C. (113° F.), boils at 190° C. (374° F.), and distills without decomposition. It has an aromatic taste and odor, dissolves sparingly in cold, abundantly in hot water, also in alcohol and ether.

It unites with bromine, forming a dibromovaleric acid, $C_5H_8Br_2O_2$, which is reconverted by sodium-amalgam into angelic acid. It is not altered by

nascent hydrogen, but when heated with concentrated *hydriodic acid* and a little phosphorus, it is converted into normal valeric acid. By fusion with *potash* it is resolved into acetic and propionic acids, a mode of decomposition which is consistent with either of the two following structural formulae of the acid :



The angelates of the alkali-metals are soluble in water and in alcohol. *Calcium angelate*, $Ca(C_4H_7O_2)_2 + Aq.$, forms shining, very soluble laminae. The *lead-salt*, $Pb(C_4H_7O_2)_2$, is a white precipitate.

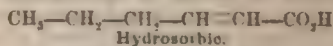
Potassium angelate treated with phosphorus oxychloride yields angelic oxide, or anhydride, $(C_4H_5O)_2O$, which is a viscid uncrystallizable oil, boiling at $240^\circ C.$ ($464^\circ F.$).

Methyl-crotonic Acid, $CH_3-CH=C\begin{smallmatrix} CH_3 \\ CO_2H \end{smallmatrix}$, formed by the action of phosphorus trichloride on ethylic methyl-ethyloxalate (p. 715), is very much like angelic acid, but melts at $62^\circ C.$ ($143.6^\circ F.$). By fusion with potash it is resolved into acetic and propionic acids.

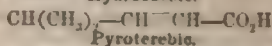
Identical with this is the so-called *tiglic acid*, which is contained as a glyceride, together with those of butyric, valeric, and other fatty acids, in the oil of *Croton Tiglium*.

Six-carbon Acids, $C_6H_{10}O_2=C_5H_9.CO_2H$.—1. *Pyroterebic acid* is formed by dry distillation of terebic acid, $C_7H_{10}O_4$ (one of the products of the action of nitric acid on turpentine-oil). It is an oily liquid, smelling like butyric acid, having a specific gravity of 1.01, and boiling at $210^\circ C.$ ($410^\circ F.$). By fusion with potash it is resolved into acetic and isobutyric acids.

2. *Hydrosorbic acid* is formed by the action of sodium-amalgam on sorbic acid, $C_6H_8O_2$. It is a liquid having a sudorific odor, a specific gravity of 0.969 at $19^\circ C.$ ($66.2^\circ F.$), and boiling at $204.5^\circ C.$ ($400.1^\circ F.$). By fusion with potash it is resolved into acetic and normal butyric acids. This and the preceding acid are therefore represented by the following formulae:—



Hydrosorbic.



Pyroterebic.

3. *Ethyl-crotonic acid*, $CH_3-CH=C\begin{smallmatrix} CH_3 \\ CO_2H \end{smallmatrix}$, is formed from the ethylic ether of diethoxalic acid (p. 715), by the action of phosphorus trichloride, or by heating with hydrochloric acid to 130° – $150^\circ C.$ (266° – $302^\circ F.$). It crystallizes in shining square prisms, has an aromatic odor, sublimes even at ordinary temperatures, and melts at $41.5^\circ C.$ ($106.7^\circ F.$). By fusion with potash it is resolved into acetic and normal butyric acids. Its salts decompose, even during the evaporation of their aqueous solutions.

Seven- to Fifteen-Carbon Acids.—*Damaluric acid*, $C_7H_{12}O_2$, and *Damolic acid*, $C_{14}H_{24}O_2$, are volatile acids, said to exist in the urine of cows and horses.—*Moringic acid*, $C_{15}H_{28}O_2$, is an oily acid, obtained, together with palmitic, stearic, and benic acids, by the saponifi-

* $n=2$, $p=0$, in formula 1, α (p. 718, footnote).

† $n=2$, $p=1$, in the same.

oil of ben (p. 713).—Cimicic acid, $C_{15}H_{25}O_2$, is a yellow crystalline acid, having a rancid odor, extracted by alcohol and ether from the bug (*Rhaphigaster punctipennis*).

Oleic Acid, $C_{18}H_{33}O_2$, is contained as a glyceride, together with erucic and arachin, in oil of earth-nut (*Arachis hypogaea*). To obtain it, the mixture of fatty acids obtained by saponifying the oil is dissolved in alcohol; the palmitic and arachidic acids are precipitated by adding lead and magnesium acetate; the filtrate is mixed with ammonia and water; the lead precipitate is decomposed by hydrochloric acid; and the filtrate hypogaeic acid is dissolved out by ether. It is also produced by oxidation of axenic acid ($C_{18}H_{25}O_2$), an acid obtained by saponification of axin, a fatty substance contained in the Mexican plant *axin*.—Hypogaeic acid crystallizes from ether in stellate groups of crystals melting at 34° or 35° C. (93.2° – 95° F.), easily soluble in alcohol and ether. Its potassium and sodium salts are soluble in water; the barium salt is soluble in hot, insoluble in cold water; the copper and silver salts are precipitated by precipitation. The ethyl ether, $C_{18}H_{33}O_2 \cdot C_2H_5$, is a yellow liquid volatile without decomposition.

Hypogaeic acid converts hypogaeic acid into the isomeric or allotropic compound, elaidic acid, related to it in the same manner as elaidic acid to oleic. It forms a colorless crystalline mass which melts at 38° C. (100° F.).

Elaidic acid, a crystalline acid obtained from sperm-oil, is identical with hypogaeic acid; it melts at 30° C. (86° F.), and boils at 28° C. (82.4° F.).

Oleic Acid, $C_{18}H_{33}O_2$.—This acid, the most important of the series, is obtained by saponification of olein, the fluid constituent of most natural fixed oils.

To obtain pure oleic acid, olive or almond oil is saponified with potash; the soap is decomposed by tartaric acid; and the separated fatty acid, after being washed, is heated for some hours in the water-bath, with half its weight of lead oxide previously reduced to fine powder. The mixture is well shaken up with about twice its bulk of ether, which dissolves the oil of lead, and leaves the stearate; the liquid, after standing for some time, is decanted and mixed with hydrochloric acid; the oleic acid is eliminated dissolves in the ether; and the ethereal solution which floats on the surface of the water is decanted, mixed with water, and freed of ether by distillation.

Large quantities of crude oleic acid are now obtained in the manufacture of tallow candles, by treating with dilute sulphuric acid the lime-soap obtained from the action of lime upon tallow. The fatty acids resulting from the decomposition are washed with hot water, and solidify in a mass of tallow; and this mass, when subjected to pressure, yields a liquid rich in oleic acid, but still retaining a considerable quantity of stearic acid. Remaining for some time in a cold place, it deposits a quantity of stearic acid, and the liquid decanted from this is sent into the market as *red oil*. It may be purified by the process just described.

Oleic acid crystallizes from alcoholic solution in dazzling white needles, melting at 14° C. (57.2° F.) to a colorless oil, which solidifies at 4° C. (39.2° F.) to a hard, white, crystalline mass, expanding considerably at the same time. Its specific gravity = 0.898 at 19° C. (66.2° F.). The acid volatilizes without decomposition. It is tasteless and inodorous, and neutral when unaltered (not oxidized), also in alcoholic solution. It is soluble in water, very soluble in alcohol, and dissolves in all proportions.

Cold strong sulphuric acid dissolves it without decomposition.

It dissolves solid fats, stearic acid, palmitic acid, etc., and is dissolved by bile, with formation of a soap and strong acid reaction.

Oleic acid, in the solid state, oxidizes but slowly in the air; but when melted, it rapidly absorbs oxygen, acquiring a rancid taste and smell and a decided acid reaction. Its decomposition by fusion with potash has been already mentioned. Chlorine and bromine, in presence of water, convert it into dichloroleic and dibromoleic acids. Bromine, added by drops to fused oleic acid, forms tribromoleic acid, $C_{18}H_{31}Br_3O_2$.

Strong nitric acid attacks oleic acid with violence, giving off red nitrous vapors, and producing volatile acids of the series $C_nH_{2n}O_2$, viz., acetic, propionic, butyric, valeric, caproic, caprylic, pelargonic, and rutic acids; also fixed acids of the series $C_nH_{2n-1}O_4$, viz., suberic, pimelic, adipic, lipic, and azelaic acids, the number and proportion of these products varying with the duration of the action.

Nitrous acid converts oleic acid into a solid isomeric or allotropic modification, called elaidic acid.

Oleates.—The formula of the neutral oleates is $M'C_{18}H_{33}O_2$, or $M'(C_{18}H_{33}O_2)_2$, according to the quantivalence of the metal: there are likewise acid oleates. The neutral oleates of the alkali-metals are soluble in water, and not so completely precipitated from their solutions by the addition of another soluble salt, as the stearates and palmitates. The acid oleates are liquid and insoluble in water. The oleates dissolve in cold absolute alcohol and in ether, a property by which they may be distinguished and separated from the stearates and palmitates.

Oleins.—Oleic acid forms three glycerides, viz., monoolein $(C_3H_5)(OH)_2(C_{18}H_{33}O_2)$; diolein $(C_3H_5)(OH)(C_{18}H_{33}O_2)_2$; and triolein $(C_3H_5)(C_{18}H_{33}O_2)_3$, which are produced by heating oleic acid and glycerin together in sealed tubes, in various proportions. The first two solidify at about $15^\circ C.$ ($59^\circ F.$).

The olein of animal fats, of olive oil, and of several other oils, both animal and vegetable, which do not dry up in the air by slow oxidation, but are converted into viscid masses having a rancid odor and acid reaction (non-drying oils), appears to be identical with triolein, but there is great difficulty in obtaining it pure. Olive oil, cooled to $4^\circ C.$ ($39^\circ F.$) or a lower temperature, deposits a large quantity of solid fat, consisting mainly of palmitin (originally called *margarin*, from its pearly lustre), and the oil filtered therefrom consists mainly of olein. A purer olein is obtained by treating olive oil with a cold strong solution of caustic soda, which saponifies the solid fats, and leaves the olein unaltered. Olein, subjected to dry distillation, yields gaseous products, liquid hydrocarbons, acrolein, and sebic acid.

Appendix to Oleic Acid.—Some non-drying oils contain the glycerides of acids homologous with oleic acid; such is the case, as already observed, with croton oil, earth-nut oil, and sperm oil. Doegling train-oil, obtained from the doegling or bottle-nosed whale (*Balena rostrata*), yields doeglic acid, $C_{19}H_{35}O_2$. Colza-oil, obtained from the seeds of certain species of *Brassica*, especially the summer rape or colza, *Brassica campestris*, var. *oleifera*, yields brassic acid, $C_{22}H_{43}O_2$; and the oil of black mustard-seed yields a similar and probably identical acid, called erucic acid.

Drying oils, such as linseed, poppy, hemp, and nut oils, contain the glycerides of linoleic acid, $C_{18}H_{31}O_2$, which may be prepared by saponifying linseed oil with potash, precipitating the aqueous solution of the resulting potassium salt with calcium chloride, dissolving out the calcium linoleate with ether, and decomposing it with hydrochloric acid. Linoleic acid is a yellowish oil of specific gravity 0.921, not altered by nitrous acid.

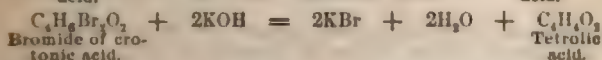
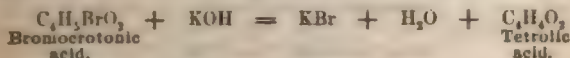
Caster oil, which is a non-drying oil, contains the glyceride of ricinoleic acid, $C_{19}H_{34}O_2$, which, when separated, forms a colorless oil, solidifying at 0° , and converted by nitrous acid into a solid modification, ricinoleaidic acid, which melts at 50° C. (122° F.). By dry distillation it is resolved into cenanthylic acid and cenanthol, and when heated with excess of caustic potash or soda, it yields secondary octyl alcohol, together with sebacic acid and free hydrogen (p. 592).

Monatomic Acids, $C_nH_{2n-4}O_2$.—The known acids of this series are.

Tetrolic acid, $C_8H_{12}O_2$
 Sorbic acid, $C_8H_{10}O_2$
 Palmitolic acid, $C_{16}H_{26}O_2$

Stearolic acid, $C_{18}H_{32}O_2$
 Behenolic acid, $C_{22}H_{40}O_2$

They are formed from the acids of the preceding series by abstraction of 2 atoms of hydrogen, which is effected by the action of alcoholic potash on the chlorine or bromine compounds or derivatives of these acids; e. g.,



They contain 4 atoms of hydrogen less than the corresponding fatty acids, and are therefore unsaturated compounds of the second order, capable of uniting with 2 or with 4 atoms of a halogen-element.

Tetrollic Acid, $C_8H_6O_2$, produced as above from monochlorocrotonic acid, crystallizes in deliquescent rhombic plates, easily soluble in alcohol and ether. It melts at 76.5° C. (169.7° F.), and boils at 203° C. (397.4° F.).

Sorbic Acid, $C_8H_{10}O_2$, occurs in the unripe berries of the mountain ash (*Sorbus aucuparia*), from which it may be obtained by mixing the juice with milk of lime and distilling. It then passes over as an oily liquid, which solidifies when boiled with strong hydrochloric acid, or when warmed with potash.

Sorbic acid crystallizes in long needles, melts at 134.5° C. (274.1° F.), decomposes when distilled alone, but is easily volatilized with vapor of water. It is nearly insoluble in cold water, but dissolves with moderate facility in hot water and in alcohol. Nascent hydrogen converts it into hydrosorbic acid, $C_8H_{10}O_2$. With bromine it forms the compounds $C_8H_8Br_2O_2$ and $C_8H_6Br_4O_2$, melting respectively at 95° C. (203° F.) and 185° C. (361.4° F.).

The metallic sorbates are crystallizable. The ammonium salt crystallizes in long needles; the barium salt, $(C_8H_7O_2)_2Ba$, and the calcium salt, $(C_8H_7O_2)_2Ca$, form silvery scales. The silver salt, $C_8H_7O_2Ag$, is a crystalline precipitate. The ethylic ether, $C_8H_7O_2 \cdot C_2H_5$, is an aromatic liquid, boiling at 195.5° C. (383.9° F.).

Palmitolic Acid, $C_{16}H_{26}O_2$, prepared from the dibromide of hypogæic acid, or of its isomeride, gaidic acid, crystallizes in shining needles which melt at 42° C. (107.6° F.). It unites with 2 and 4 atoms of bromine, but is not altered by nascent hydrogen.

Stearolic Acid, prepared in like manner from the dibromide of oleic or elaidic acid, crystallizes in long prisms, which melt at 4° C. (118.4° F.) and distil almost without decomposition. It is insoluble in water, but dissolves readily in alcohol and ether. It unites with 2 and 4 atoms of *amine*, but is not altered by nascent hydrogen. By carefully regulated fusion with *potash*, it is resolved into acetic and hypogaeic acids; at high temperatures myristic acid is produced.

Behenolic Acid, $C_{22}H_{40}O_2$, from dibromide of erucic or brassic acid (p. 721), forms shining needles, melting at 75° C. (167° F.).

The last three acids, heated with fuming nitric acid, are converted into monobasic acids of the form $C_nH_{2n-4}O_4$, viz.:—

Palmitoxylie.



Stearoxylie.



Behenoxylie.

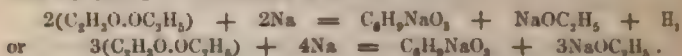


melting at 67° C. (162.6° F.), 86° C. (186.8° F.), 90° C. (194° F.).

These acids crystallize in shining plates or scales.

CARBOKETONIC ACIDS.

These acids are derived from ethyl acetate and other compound ethers of the fatty series. When sodium is heated with ethyl acetate, it dissolves, with little or no evolution of hydrogen, and the whole solidifies on cooling to a crystalline mass of sodium ethylate and ethylic acetosodacetate, $C_4H_7NaO_3$. The reaction is either

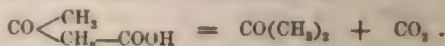


The quantity of hydrogen evolved in this reaction varies considerably according to the temperature and pressure under which it takes place, and the proportions of the materials used; sometimes no gas is evolved, showing that the reaction takes place according to the second equation, and under no circumstances yet observed is the quantity of hydrogen given off exactly equivalent to the sodium dissolved, as it should be if the reaction took place entirely according to the first equation. It is most probable, therefore, that the two reactions generally take place together.

Ethylic acetosodacetate (Wanklyn's *sodium-triacetyl*) crystallizes in shining scales. When treated with acetic acid, it is converted into the

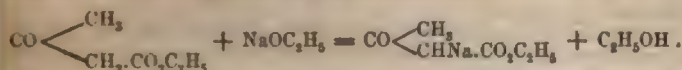
compound $C_6H_{10}O_3$ or $CO \begin{smallmatrix} CH_3 \\ \diagup \\ CH_2-CO-OC_2H_5 \end{smallmatrix}$, which is the ethylic ether of aceto-acetic acid, $CO \begin{smallmatrix} CH_3 \\ \diagup \\ CH_2-CO-OH \end{smallmatrix}$, derived from acetic acid,

$CO \begin{smallmatrix} CH_3 \\ \diagup \\ OH \end{smallmatrix}$, by substitution of acetyl, CH_3CO , for one of the hydrogen-atoms in the methyl group. This acid is not known in the free state; when separated from its ether by boiling with alkalis or acids, it is resolved into acetone and carbon dioxide,



The ethylic ether, $C_6H_{10}O_3$ (also called ethyl-diacetic acid), is a liquid having an odor of strawberries, a specific gravity of 1.03, and boiling at 160.8° C. (357.5° F.). By the action of sodium or of sodium ethyl-

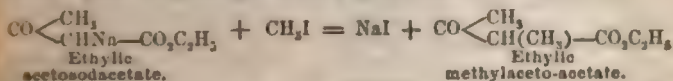
It is converted into ethylic acetosodacetate, the compound already mentioned as a direct product of the action of sodium on acetic ether:—



The potassium salt is obtained in a similar manner. The barium salt, $(C_6H_5O)_2Ba$, obtained by dissolving the ether in baryta-water, is easily soluble in water. From its solution the corresponding salts of the heavy metals may be obtained by double decomposition.

Methylic Aceto-acetate, $C_5H_8O_3 = CO \begin{matrix} \nearrow CH_3 \\ \searrow CH_2.CO_2CH_3 \end{matrix}$, obtained by the action of sodium on methyl acetate, etc., is a colorless, pungent-smelling liquid, which boils at $170^\circ C.$ ($338^\circ F.$), and has a specific gravity of 1.037 at $9^\circ C.$ ($48.2^\circ F.$). It has a faint acid reaction, dissolves sparingly in water, freely in alcohol and ether; produces a dark-red coloration with ferric chloride; is resolved by boiling with hydrochloric acid or with alkalis, into acetone, carbon dioxide, and methyl alcohol. Its sodium salt, $C_5H_7O_3Na$, crystallizes in shining needles. The barium salt, $(C_5H_7O_3)_2Ba$, is obtained by dissolving the ether in baryta-water. Its aqueous solution mixed with cupric acetate yields the copper salt $(C_5H_7O_3)_2Cu + 2H_2O$ in green crystals, slightly soluble in water.

By treating the sodium derivatives of these aceto-acetic ethers with the halides of alcohol-radicles, new ethers are obtained, in which the sodium of the original compound is replaced by an alcohol-radicle, *e. g.*,



Ethyllic
acetopodacetal.

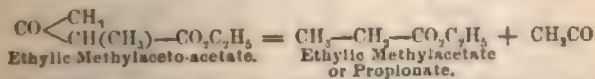
Ethyllic
methylaceto-acetate.

In these last ethers an atom of hydrogen may also be replaced by sodium, by the action of metallic sodium or of sodium ethylate, producing compounds like

Ethyllic Sodio-methylaceto-acetate, $\text{CO} \begin{matrix} \text{CH}_3 \\ \diagup \\ \text{CNa}(\text{CH}_3) \end{matrix} - \text{CO}_2\text{C}_2\text{H}_5$; and in these again the sodium may be replaced by alcohol-radicles, yielding, for example,

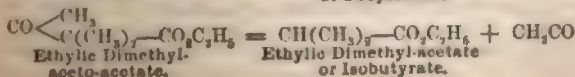
Ethyl Methylthyl-aceto-acetate, $\text{CO} \begin{matrix} \text{CH}_3 \\ \diagup \\ \text{C}(\text{CH}_3)(\text{C}_2\text{H}_5) \end{matrix} \text{—CO, C}_2\text{H}_5$.

Lastly, these mono- and di-substituted aceto-acetic ethers, when heated alone, or better, with sodium ethylate, or with ethylic sodio-aceto-acetate, $C_4H_7NaO_2$, are resolved into the group C_2H_5O or $CH_3.CO$ (which, by polymerization, yields dehydracetic acid, $C_6H_4O_3$), and substituted acetic ethers, that is to say, ethers of the higher fatty acids; e. g.,



Ethyllic Methylaceto-acetate.

**Ethyllic Methylacetate
or Propionate.**

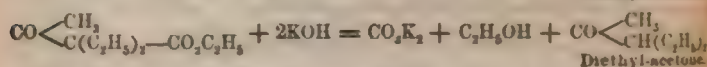
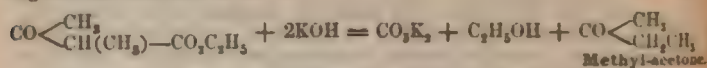


Ethyllic Dimethyl-
aceto-acetate.

**Ethylis Dimethyl-acetate
or Isobutyrate.**

This reaction explains the direct production of the ethers of the higher fatty acids by the simultaneous action of sodium and alcoholic-radicles on acetic ether (p. 686).

The substituted ethers of aceto-acetic acid, heated with aqueous alkalis, are decomposed in the same manner as ethylic aceto-acetate (p. 722), yielding various ketones; e. g.,



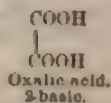
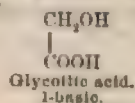
The following table exhibits the boiling points and specific gravities of these substituted acetacetic ethers, and their reactions with ferric chloride:

| | Boiling Point. | Spec. Gravity. | Reaction with Ferric Chloride |
|--|---|--|-------------------------------|
| $\text{CO} \begin{array}{l} \text{CH}_3 \\ \diagup \text{CH}(\text{CH}_3) \end{array} - \text{CO}_2\text{CH}_3$ | $\left\{ \begin{array}{l} 177^\circ \text{ C.} \\ (350.6^\circ \text{ F.}) \end{array} \right.$ | 1.020 at 9° C.
(48.2° F.) | Violet-red. |
| $\text{CO} \begin{array}{l} \text{CH}_3 \\ \diagup \text{CH}(\text{C}_2\text{H}_5) \end{array} - \text{CO}_2\text{CH}_3$ | $\left\{ \begin{array}{l} 190^\circ \text{ C.} \\ (374^\circ \text{ F.}) \end{array} \right.$ | 0.995 at 14° C.
(57.2° F.) | Violet-red. |
| $\text{CO} \begin{array}{l} \text{CH}_3 \\ \diagup \text{CH}(\text{CH}_3) \end{array} - \text{CO}_2\text{C}_2\text{H}_5$ | $\left\{ \begin{array}{l} 186^\circ \text{ C.} \\ (366.8^\circ \text{ F.}) \end{array} \right.$ | | |
| $\text{CO} \begin{array}{l} \text{CH}_3 \\ \diagup \text{C}(\text{CH}_3)_2 \end{array} - \text{CO}_2\text{C}_2\text{H}_5$ | $\left\{ \begin{array}{l} 184^\circ \text{ C.} \\ (363.2^\circ \text{ F.}) \end{array} \right.$ | 0.991 at 16° C.
(60.8° F.) | |
| $\text{CO} \begin{array}{l} \text{CH}_3 \\ \diagup \text{CH}(\text{C}_2\text{H}_5) \end{array} - \text{CO}_2\text{C}_2\text{H}_5$ | $\left\{ \begin{array}{l} 195^\circ \text{ C.} \\ (383^\circ \text{ F.}) \end{array} \right.$ | 0.983 at 16° C.
(60.8° F.) | Blue. |
| $\text{CO} \begin{array}{l} \text{CH}_3 \\ \diagup \text{C}(\text{C}_2\text{H}_5)_2 \end{array} - \text{CO}_2\text{C}_2\text{H}_5$ | $\left\{ \begin{array}{l} 210-212^\circ \text{ C.} \\ (410-413^\circ \text{ F.}) \end{array} \right.$ | 0.974 at 0° C. | |

Isopropylated acetacetic ethers are obtained by treating the acetacetic ethers with sodium and isopropyl iodide.

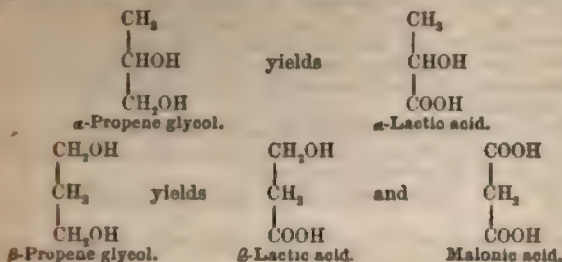
Diatomic Acids.

These acids contain two hydroxyl groups, and are monobasic or bibasic, according as one or both of these hydroxyls belongs to a carboxyl group, COOH ; e. g.,

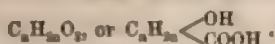


Some of them are formed by oxidation (exchange of H_2 for O), from diatomic alcohols (glycols), containing the same number of carbon-atoms, those glycols which contain the group CH_2OH twice, yielding in this manner two diatomic acids, one mono- and the other bibasic, while those which

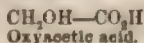
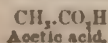
contain this group only once, yield only one acid, which is monobasic; thus:—



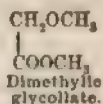
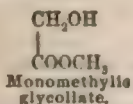
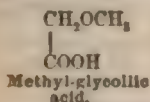
1. MONOBASIC ACIDS.



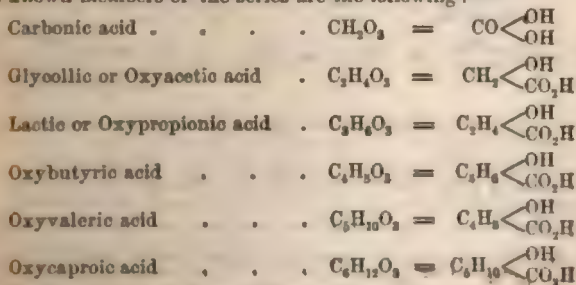
These acids are called lactic acids, after the most important member of the series, and oxy-fatty acids, because they may be derived from the acids $\text{C}_n\text{H}_{2n}\text{O}_2$ by substitution of OH for H; thus:—



They contain two hydroxyl groups, one alcoholic (connected with the radicle C_nH_{2n}), and having its hydrogen replaceable by monatomic alcohol-radicles, acid radicles, and alkali-metals; the other, basic (connected with CO), and having its hydrogen replaceable by metals in general to form salts. Each of them can, therefore, form three ethers, containing monatomic alcohol-radicles, but only one series of metallic salts, except with the alkali-metals, with each of which they can form two salts. Of the ethers, one is acid and the other two are neutral; thus from glycollic acid, $\text{CH}_2\text{OH}.\text{COOH}$, are formed:—



The known members of the series are the following:—



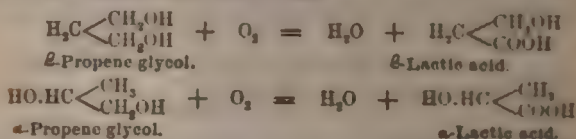
and others containing 7, 9, and 12 atoms of carbon.

All those acids of the series which contain more than two atoms of carbon admit of isomeric modifications. Of these some are analogous in structure to the primary or secondary alcohols, and are called *normal* or *iso*-acids, according to the structure of the alcohol-radicles contained in them. Others are analogous in structure to the tertiary alcohols, and are formed from oxalic acid or its ethers by a series of transformations to be presently explained.

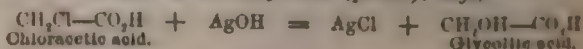
They are all monobasic, as already observed, except carbonic acid, which is bibasic, its two hydroxyl groups being similarly related to the group CO. This acid will be considered by itself.

The *normal* and *iso*-lactic acids are formed by the following general processes:—

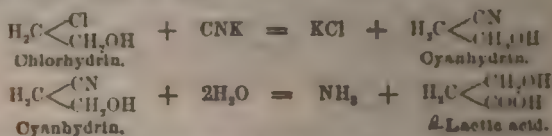
1. By slow oxidation of the glycols in contact with platinum black, or by the action of dilute nitric acid; *e. g.*,



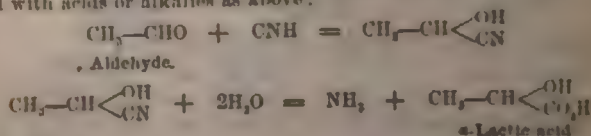
2. By the action of moist silver oxide on the monochlorinated or monobrominated derivatives of the fatty acids (p. 689); *e. g.*,



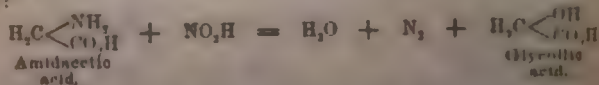
3. From the glycollic chlorhydrins (p. 599), by converting them into cyanides by the action of potassium cyanide, and boiling the resulting cyanides with alkalis or acids:



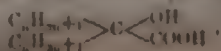
4. By heating an aldehyde or a ketone with hydrocyanic and hydrochloric acid, whereby a cyanhydrin is produced, and treating this compound with acids or alkalis as above:



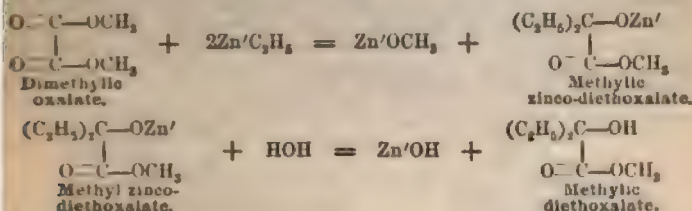
5. By the action of nitrous acid on the amidated derivatives of the fatty acids:



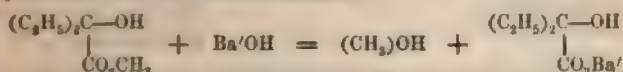
The *tertiary lactic acids* are represented by the general formula;



are obtained in the form of ethers by the action of the zinc-compound on alcohol-radicle, C_nH_{2n+1} , on a neutral ether of oxalic acid containing radicle of the same series, such as diethylic oxalate. The reaction consists in the replacement of an atom of oxygen in the oxalic ether by two equivalents of alcohol-radicle, and the simultaneous replacement of an equivalent of ethyl, methyl, etc., in the oxalic ether by an equivalent* of zinc, whereby an ether of zinc-diethoxalic acid, etc., is produced, which can then be converted into the required acid; thus:



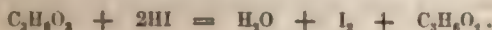
The methylic diethoxalate is easily decomposed by baryta-water, yielding ethyl alcohol and barium diethoxalate:



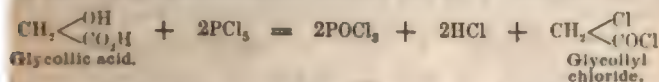
If this salt decomposed by sulphuric acid yields diethoxalic acid, $\text{H}_2\text{C}(\text{OH})_2$, isomeric with lactic acid.

In the first stage of the process, it is found better to use a mixture of ethyl iodide with metallic zinc, which produces zinc ethide, instead of the latter compound previously prepared. The other tertiary lactic acids are prepared in a similar manner.

Reactions.—1. All the acids of the series, $C_nH_{2n+1}O_3$, are reduced by hydriodic acid to the corresponding monatomic acids, $C_nH_{2n+1}O_2$, e. g., lactic to propionic acid:



By the action of phosphorus pentachloride, both their hydroxyl groups are replaced by chlorine; thus glycollic acid yields glycollyl chloride, or chloroacetyl chloride, $\text{CH}_2\text{Cl.CO.Cl}$:

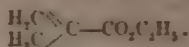


The chlorine in the group COCl of the resulting chlorides is easily attacked by water and alcohols, forming acids or ethers: chloroacetyl chloride, for example, yielding chloroacetic acid, $\text{CH}_2\text{Cl.CO.OH}$, or its ethers.

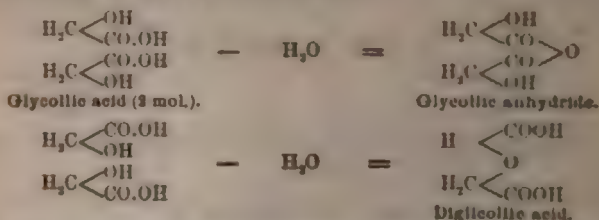
2. The ethers of the tertiary lactic acids, when treated with PCl_5 or POCl_3 , are converted (by abstraction of H_2O) into ethers of the acrylic series

* To simplify the equations, the equivalent of zinc ($\text{Zn}'=32.5$) is used instead of the atom (65).

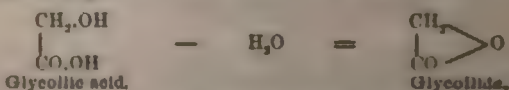
(p. 714), *e. g.*, ethylic dimethoxalate, $(\text{CH}_3)_2\text{COH}-\text{CO}_2\text{C}_2\text{H}_5$, into ethylic methylaerylate,



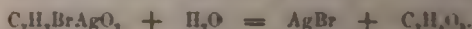
3. The isolactic acids, when deprived of the elements of water by the action of heat or otherwise, are converted into anhydrides, which may be of three kinds. If the elements of 1 mol. H_2O , are removed partly from one and partly from another molecule of the acid, and the two residues unite, the result is an anhydride of the first order, differing in constitution and properties according as the two hydrogen-atoms are taken from the carboxyl-groups, or from the alcoholic hydroxyls; in the former case, the product is an acid anhydride; in the latter, an alcoholic anhydride, or anhydro-acid; thus:



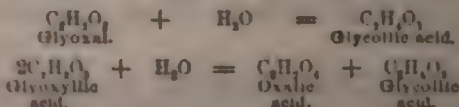
If, on the other hand, one molecule of water is removed from one molecule of the acid, the remainder constitutes an anhydride of the second order; *e. g.*:



Glycollic Acid, $\text{C}_2\text{H}_3\text{O}_3 = \text{CH}_2 \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{CO}_2\text{H} \end{array}$.—This acid is produced in a variety of reactions, some of which have been already mentioned, viz. the oxidation of glycol by contact with platinum black or by treatment with dilute nitric acid; the decomposition of amidaacetic acid (glycine) by nitrous acid; the action of water or alkalis on bromoacetic and chloroacetic acid, or their salts (p. 690), *e. g.*, by boiling silver bromoacetate with water:



It is also produced: *a.* By the action of alkalis on glyoxal and glyoxylic acid.



b. Together with glyoxal, glyoxylic acid, and other products, by the action of nitric acid upon alcohol.

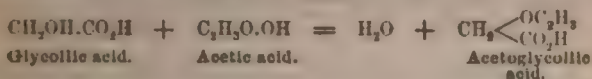
c. By the action of nascent hydrogen (evolved by zinc and sulphuric acid) upon oxalic acid:



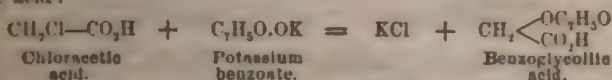
Glycollic acid differs somewhat in its properties, according to the manner in which it is prepared, being sometimes syrupy and uncrystallizable, sometimes separating from its solution in ether in large regular crystals. It has a very sour taste, dissolves easily in water, alcohol, and ether; melts at 78° or 79° C. (172.4° – 174.2° F.); begins to boil at 100° ; decomposes when heated to above 150° C. (302° F.). All the glycollates are more or less soluble and crystallizable.

The *calcium salt*, $(C_2H_3O_2)_2Ca + 2H_2O$, is slightly soluble in cold water, and crystallizes in needles. The *silver salt*, $C_2H_3O_2Ag + \frac{1}{2}H_2O$, is also sparingly soluble. The *ethylic ether*, $C_2H_5O_2.C_2H_5$, is a liquid having a specific gravity of 1.03, and boiling at 150° C. (302° F.).

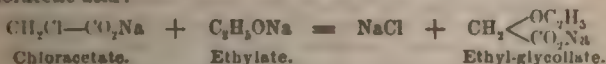
Acid and Alcoholic Derivatives of Glycollic Acid.—The alcoholic hydrogen of glycollic acid may be replaced either by acid or by alcoholic radicals. The acid derivatives are formed: a. By heating glycollic acid with monatomic acids:



b. By the action of the alkali-salts of monatomic acids on monochloroacetic acid:

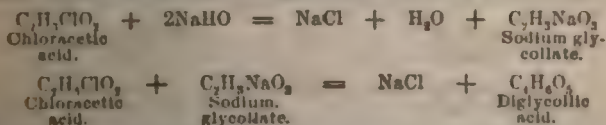


The alcoholic derivatives are formed by the action of sodium alcoholates on chloroacetic acid:



Methyl-glycollic acid, $CH_3OCH_2.CO_2H$, boils at 198° C. (384.4° F.); *ethyl-glycollic acid*, $CH_3OC_2H_5.CO_2H$, at 206° C. (402.8° F.). Both are permanent in the air, and are not decomposed by boiling with alkalis.

Anhydrides.—Diglycollic acid, $C_4H_6O_5 = 2C_2H_3O_2 - H_2O =$
 $O \begin{array}{l} \diagup CH_2-COOH \\ \diagdown CH_2-COOH \end{array}$, also called *Paramalic acid*.—This acid, isomeric with malic acid, and related to glycollic acid in the same manner as diethenic alcohol to glycol, is produced by the dehydration of glycollic acid, and by the oxidation of diethenic or triethenic alcohol. It is also formed in the preparation of glycollic acid by heating sodium chloroacetate with caustic soda, which in fact is the process by which it was first obtained:



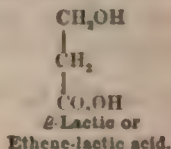
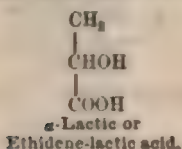
Diglycollic acid crystallizes in large rhombic prisms, melting at 150° C. (302° F.), and distilling with slight decomposition at 250° C. (482° F.); easily soluble in water and in alcohol; not decomposed by boiling with alkalis. It is bibasic, forming with univalent metals, acid salts containing $C_4H_3M'O_5$, and normal salts, $C_4H_4M'_2O_5$; with bivalent metals it forms only normal salts, $C_4H_4M''O_5$. The *calcium salt* is very soluble.

Glycollic Anhydride, $C_2H_2O_3 = O \begin{matrix} \diagup CO-CH_2OH \\ \diagdown CO-CH_2OH \end{matrix}$, obtained by exposing the acid for a few days to the vapors of sulphuric anhydride, is a lustreless powder, melting at $128^\circ - 130^\circ C.$ ($262.4^\circ - 266^\circ F.$); insoluble in alcohol, ether, and cold water; boiling water reconverts it into glycollic acid and dissolves it.

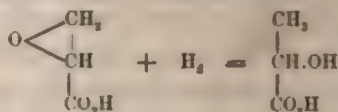
Glycollide, $C_2H_2O_3 = O \begin{matrix} \diagup CH_2 \\ \diagdown CO \end{matrix}$, is formed by heating glycollic acid to $150^\circ C.$ ($302^\circ F.$). It is a white amorphous powder, melting at $180^\circ C.$ ($356^\circ F.$), insoluble in cold water, reconverted into glycollic acid by boiling with water. Heated with ammonia it yields glycollamide, $CH_2OH-CONH_2$.

Lactic or Oxypropionic Acids, $C_3H_4O_3 = C_2H_3 \begin{matrix} \diagup OH \\ \diagdown CO.OH \end{matrix}$.

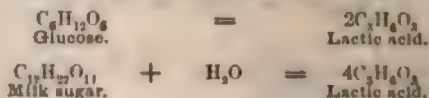
—Of these acids there are two isomeric modifications, viz. :—



1. **Ethidene-lactic, or Isolactic Acid,** $HOHC \begin{matrix} \diagup CH_3 \\ \diagdown CO_2H \end{matrix}$, is the ordinary lactic acid produced by a peculiar fermentation of sugar and other carbohydrates, hence called *fermentation lactic acid*. It is also produced by the first, second, fourth, and fifth of the general reactions already mentioned (p. 726), viz., by oxidation of α -propene-glycol; by the action of moist silver oxide on α -chloropropionic acid; by the action of hydrocyanic and hydrochloric acid on aldehyde; and by that of nitrous acid on α -amidopropionic acid (alanine); and lastly, by the action of nascent hydrogen on pyruvic acid :—



Preparation of Ordinary Lactic Acid by Fermentation.—Various kinds of sugar and dextrin, when subjected to the action of particular ferments, are converted into lactic acid, the change consisting in a resolution of the molecule, preceded in some cases by the assumption of the elements of water :—



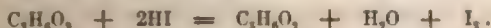
This lactous fermentation requires a temperature between 20° and $40^\circ C.$ (68° and $104^\circ F.$), and the presence of water and certain ferments—viz., albuminous substances in a peculiar state of decomposition, such as casein, gluten, or animal membranes, especially the coating of the stomach of the calf (rennet), or of the dog, or bladder. According to Pasteur and others, it depends upon the presence of a peculiar fungus, *Penicillium glaucum* (p.

The following is a good method for preparing the acid in considerable quantity: 2 gallons of milk are mixed with 6 pounds of raw sugar, 4 pints of water, 8 ounces of putrid cheese, and 4 pounds of chalk, which should be mixed up to a creamy consistence with some of the liquid. This mixture is exposed in a loosely covered jar to a temperature of about 30° (80° F.), with occasional stirring. The use of the chalk is to neutralize lactic acid, which would otherwise coagulate the casein, render it insoluble, and thereby put a stop to the process. At the end of two or three days it will be found converted into a semi-solid mass of calcium lactate, which may be drained, pressed, and purified by re-crystallization from ether. The lactate may be decomposed by the necessary quantity of pure dilic acid, the filtered liquor neutralized with zinc carbonate, and, after second filtration, evaporated until the zinc-salt crystallizes out on cooling. If, in the first part of the process, the solid calcium lactate be not removed at the proper time from the fermenting liquid, it will gradually dissolve and disappear, being converted into soluble butyrate (p. 703). An important modification of this process consists in employing commercial α -white instead of powdered chalk, which yields at once difficultly soluble zinc lactate, easily purified by recrystallization. The zinc lactate may, lastly, be redissolved in water and decomposed by sulphuretted hydrogen, in order to obtain the free acid. Together with the lactic acid a small quantity of mannite is invariably formed. This is separated by extracting the concentrated aqueous solution with ether, in which the lactic acid alone is soluble.

Lactic acid may be extracted from a great variety of liquids containing decomposing organic matter, as *sauerkraut*, a preparation of white cabbage, the sour liquor of the starch-maker, etc.

Solution of lactic acid may be concentrated in the vacuum of the air-bath, over a surface of oil of vitriol, until it appears as a colorless, syrupy liquid, of sp. gr. 1.215. It has an intensely sour taste and acid reaction: it is hygroscopic, and very soluble in water, alcohol, and ether. By prolonged evaporation over sulphuric acid it is partly resolved into ether and anhydride, and by distillation it splits up into lactide, $C_2H_4O_3$, ethyde, carbon monoxide, and water.

By oxidation with chromic acid mixture lactic acid yields formic and acetic acids. Boiled with dilute nitric acid, or with dioxide of lead or titanium, it is converted into oxalic acid. Distilled with dilute sulphuric acid and dioxide of lead or manganese, it yields a large quantity of aldehyde, together with carbon dioxide. Hydriodic acid, or a mixture of phosphorus triiodide and water, reduces it to propionic acid, with liberation of iodine:



By heating with hydrobromic acid it is converted into α -bromo-propionic acid:



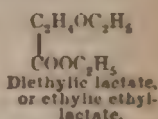
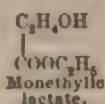
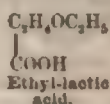
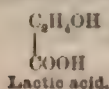
Lactates.—The best defined of these salts are represented by the formulae, $M'C_2H_3O_3$ and $M''(C_2H_3O_3)_2$. Barium and calcium also form acid lactates, e. g., $Ca(C_2H_3O_3)_2 \cdot 2C_2H_5O_3$. The lactates are, for the most part, sparingly soluble in cold water, and effloresce rapidly from their solutions: they are all insoluble in ether. When heated with excess of strong sulphuric acid, they give off a large quantity of pure carbon monoxide.

Sodium lactate, $C_2H_3O_3Na = CH_3-CH \begin{smallmatrix} OH \\ CO_2Na \end{smallmatrix}$, obtained by neutralizing lactic acid with sodium carbonate, is an amorphous mass, which, when heated

with metallic sodium is converted into disodic lactate, $\text{CH}_3\text{C} \begin{smallmatrix} \text{ONa} \\ \text{CO}_2\text{Na} \end{smallmatrix}$, the alcohol hydrogen being likewise replaced by sodium.

Calcium lactate, $(\text{C}_3\text{H}_5\text{O}_2)_2\text{Ca} + 5\text{H}_2\text{O}$, is obtained in the fermentation process above described, or by boiling aqueous lactic acid with calcium carbonate. It dissolves in 9.5 parts of water at ordinary temperatures.—*Zinc lactate*, $(\text{C}_3\text{H}_5\text{O}_2)_2\text{Zn} + 3\text{H}_2\text{O}$, gives off its water quickly at 100°C , dissolves in 6 parts of boiling water, in 5.8 parts of cold water, and is nearly insoluble in alcohol.—*Ferrous lactate* is precipitated in small yellowish needles on mixing ammonium lactate with ferrous chloride or sulphate.—*Ferric lactate* is a brown deliquescent mass.

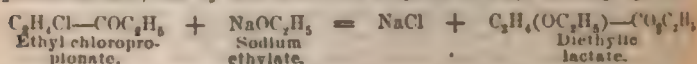
Lactic Ethers.—Lactic acid, like the other members of the group, can form three different ethers containing the same univalent alcohol-radicle, according as the alcoholic or the basic hydrogen-atom, or both, are replaced; thus:



Monethyllic lactate, $\text{C}_3\text{H}_5\text{O}_2\cdot\text{C}_2\text{H}_5$, is produced by distilling potassium or sodium lactate with potassium ethylsulphate. It is a syrupy liquid, boiling at 176°C . (348.8°F .). Potassium dissolves in it, with evolution of $\text{C}_2\text{H}_5\text{OK}$

hydrogen, forming ethylic potassiolactate, $\begin{array}{c} | \\ \text{COOC}_2\text{H}_5 \end{array}$ —*Ethyl-lactic*

acid, $\text{C}_2\text{H}_5(\text{OC}_2\text{H}_5)\text{—CO}_2\text{H}$, is obtained as a potassium or calcium salt by decomposing diethyllic lactate with potash or milk of lime. When separated from these salts by sulphuric acid, it forms a viscid liquid, boiling with partial decomposition between 195° and 198° .—*Diethyllic lactate*, $\text{C}_2\text{H}_5(\text{OC}_2\text{H}_5)_2\text{—CO}_2\text{C}_2\text{H}_5$, is produced by the action of ethyl-iodide on ethyl potassiolactate, and by that of sodium ethylate on ethyl chloropropionate.



Methyl-lactic acid, $\text{C}_3\text{H}_5(\text{CH}_3)\text{O}_2$, and its zinc and silver salts have also been obtained.

The alcoholic hydrogen of lactic acid may also be replaced by acid radicals, forming such compounds as acetolactic acid, $\text{C}_2\text{H}_5\text{C} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{CO}_2\text{H} \end{smallmatrix}$.

Lactyl Chloride, $\text{C}_2\text{H}_5(\text{OCl})_2$, or *α -Chloropropionyl Chloride*, $\text{C}_2\text{H}_4\text{Cl—COCl}$, is obtained, together with phosphorus oxychloride, by gently heating a mixture of calcium lactate with phosphorus pentachloride. It is a colorless liquid, boiling above 100° , and decomposed by water, forming hydrochloric and chloropropionic acids. With alcohol it forms ethylic α -chloropropionate. By heating with alkalis it is converted into lactic acid.

LACTIC ANHYDRIDES.—1. Dilactic acid, $\text{C}_6\text{H}_{10}\text{O}_5 = 2\text{C}_3\text{H}_5\text{O}_2 - \text{H}_2\text{O} = \begin{array}{c} \text{H}_3\text{C—CH—CO}_2\text{H} \\ | \quad \diagup \\ \text{O} \quad \text{OC}_2\text{H}_5 \\ | \quad \diagdown \\ \text{H}_3\text{C—CH—CO}_2\text{H} \end{array}$, formed by heating lactic acid to $130^\circ\text{--}200^\circ\text{C}$. ($266^\circ\text{--}392^\circ\text{F}$.), is an amorphous mass, very bitter, and nearly insoluble in water, but reconverted into lactic acid by prolonged boiling with water.

2. Lactide, $C_4H_4O_3 = HC-CH_2$, the second anhydride of lactic acid,

is obtained by distillation of lactic or dilactic acid, and may be obtained pure by evaporating the distillate, washing the residue with cold alcohol, and crystallizing it from hot alcohol. Lactide thus purified crystallizes in rhombic plates which melt at $107^\circ C.$ ($224.6^\circ F.$); it dissolves gradually in water.

Paralactic or Sarcolactic acid is a modification of lactic acid, existing in the animal organism, especially in muscular flesh, from which it may be extracted by cold water or dilute alcohol. It is most easily prepared from Liebig's extract of meat. It agrees in all its reactions with fermentation lactic acid, and must therefore have the same chemical structure—that is to say, it must be an ethidene-lactic acid—but it differs from ordinary lactic acid in its relation to polarized light, inasmuch as it turns the plane of polarization to the left, whereas ordinary lactic acid is optically inactive. Hence it is inferred that the two modifications, though chemically identical, differ from one another in physical structure; in other words, that the difference between them consists, not in the arrangement of the atoms within the molecules, but in the arrangement or modification of the molecules amongst themselves. There are other cases of difference in physical character coexisting with chemical identity, which are attributed to a similar difference of physical structure, as in the several modifications of turpentine oil.

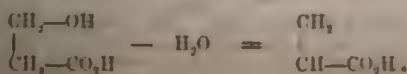
Some of the paralactates differ from the ordinary lactates in solubility and other characters; thus:

| | Lactate. | Paralactate. |
|----------------|--|---|
| Calcium Salts. | $(C_3H_5O_3)_2Ca + 5H_2O$; nodular groups of needles, soluble in 9.5 parts of cold water. | $+4H_2O$; soluble in 12 parts of cold water. |
| Zinc Salts. | $(C_3H_5O_3)_2Zn + 3H_2O$; slender needles, soluble in 58 parts of cold water. | $+2H_2O$; thick shining prisms, soluble in 17 parts of water at $15^\circ C.$ ($59^\circ F.$). |

Paralactic acid heated to $130^\circ C.$ ($266^\circ F.$) yields dilactic acid, convertible by water into ordinary lactic acid.

2. Ethene-lactic or Hydracrylic Acid, $\begin{array}{c} CH_2-OH \\ | \\ CH_2-CO_2H \end{array}$.—This acid is

produced by heating β -iodopropionic acid with moist silver oxide; $CH_2I-CH_2-CO_2H + AgOH = AgI + CH_2OH-CH_2-CO_2H$. It is a thick, uncrystallizable syrup, which, when heated alone or boiled with sulphuric acid diluted with an equal weight of water, is converted by dehydration into acrylic acid:



By heating with hydriodic acid, it is reconverted into *l*-iodopropionic acid; by oxidation with chromic acid mixture, or nitric acid, it yields oxalic acid and carbon dioxide. When heated with silver oxide it is converted into carbacetoxylic acid, $C_3H_3O_4$.

The metallic hydraerylates are crystallizable. The *sodium salt*, $C_3H_3O_2Na$, crystallizes in flat prisms, which melt without loss of weight at 142° – 145° C. (287.6° – 298.4° F.), but give off water at 156° C. (302° F.), leaving sodium acrylate, $C_3H_3O_2Na$. The *calcium salt* $(C_3H_3O_2)_2Ca + 2H_2O$, forms large rhombic prisms, which give off their water of crystallization at 100° C. The dehydrated salt unites without alteration at 140° – 145° C. (284° – 293° F.), but at 190° C. (374° F.) it gives off water, and is converted into acrylate $(C_3H_3O_2)_2Ca - 2H_2O = (C_3H_3O_2)_2Ca$. The *zinc salt*, $(C_3H_3O_2)_2Zn + 4H_2O$, crystallizes from a moderately strong solution in large shining prisms, soluble in an equal weight of water at 15° C. (59° F.).*

Oxybutyric Acids, $C_4H_5O_3 = C_3H_4 \begin{smallmatrix} OH \\ \diagup \\ CO_2H \end{smallmatrix}$.—Five of these acids are theoretically possible, and four are known.

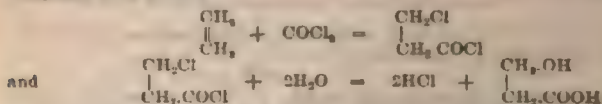
1. *α-Oxybutyric acid*, $CH_3-CH_2-CHOH-CO_2H$, is formed by heating *α*-bromobutyric acid with moist silver oxide, or with aqueous potash. It is crystalline, very deliquescent, and melts at 43° – 44° C. (109.4° – 111.2° F.). Its salts are crystalline, the zinc-salt, $(C_4H_5O_3)_2Zn$, forming white laminae, slightly soluble in cold water.

2. *β-Oxybutyric acid*, $CH_3-CHOH-CH_2-CO_2H$, is produced by boiling *β*-bromobutyric acid with silver oxide: by the action of sodium amalgam on ethylic aceto-acetate:



by the oxidation of aldol, $CH_3-CHOH-CH_2-CHO$ (p. 675); and apparently also by heating propene-chlorhydrin, $CH_3-CHOH-CH_2Cl$, with potassium cyanide, whereby it is converted into the corresponding cyanhydrin, and saponifying the latter with potash. The free acid is an in-crystallizable syrup; the calcium salt, $(C_4H_5O_3)_2Ca$, crystallizes with difficulty. The acid obtained from propene-chlorhydrin is resolved by distillation into water and solid crotonic acid, $CH_3-CH=CH-CO_2H$.

* According to Wislicenus (Liebig's *Annalen*, clix. 6), hydraerylic acid prepared from *l*-iodopropionic acid is not identical with ethene-lactic acid prepared by combining ethene with carbonyl chloride (phosgene), and decomposing the resulting compound with water:



The ethene-lactic acid thus obtained is converted by oxidation with chromic acid or nitric acid into malonic acid, $COOH-CH_2-COOH$, whereas hydraerylic acid, as above stated, is resolved thereby into oxalic acid and carbon dioxide. Moreover, the salts of hydraerylic acid are crystalline, whereas those of ethene-lactic acid are amorphous. To account for these differences, Wislicenus assigns to hydraerylic acid the formula, $CH_2OH-CHOH-CHOH$, and corresponding formula to

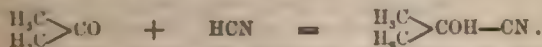


l-Iodopropionic acid and acrylic acid. These formulæ, however, are somewhat improbable, as they do not contain the group $COOH$; moreover, the formation of ethene-lactic acid from ethene in the manner described by Wislicenus does not appear to be well established. (See Watts's Dictionary of Chemistry, 2d Suppl., 716.)

3. *γ-Oxybutyric acid*, or *Normal Oxybutyric acid*, $\text{CH}_3\text{OH}-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{H}$, is prepared from succinic acid, $\text{CHO}-\text{CH}_2-\text{CH}_2-\text{CHO}$.

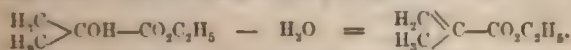
4. *Oxyisobutyric acid*, $\text{H}_3\text{C}>\text{COH}-\text{CO}_2\text{H}$, is produced :

a. By the action of hydrocyanic and hydrochloric acids on acetone ; hence *acetal acetic acid* :



β. From ethyl oxalate by the action of methyl iodide and zinc (p. 714) : hence called *dimethyloxalic acid*. γ. From bromoisobutyric acid, $(\text{CH}_3)_2\text{CH}-\text{CO}_2\text{H}$, by boiling with baryta-water. δ. By oxidation of isopentene glycol (p. 608).

Oxyisobutyric acid crystallizes in slender prisms, soluble in water and in ether. It sublimes at 50°C . (122°F .), melts at 79°C . (174.2°F .), and distils at 212°C . (413.6°F .). Its ethylic ether, treated with phosphorus trichloride, is converted into ethylic methylacrylate :



By oxidation with chromic acid mixture, oxyisobutyric acid is resolved into carbon dioxide and acetone. Its *barium salt*, $(\text{C}_4\text{H}_7\text{O}_3)_2\text{Ba}$, forms shining needles, easily soluble in water. The *zinc salt*, $(\text{C}_4\text{H}_7\text{O}_3)_2\text{Zn} + 2\text{H}_2\text{O}$, crystallizes in shining six-sided prisms or tables, sparingly soluble in cold water.

Oxyvaleric Acids, $\text{C}_5\text{H}_{10}\text{O}_3 = \text{C}_4\text{H}_9\text{C}(\text{OH})(\text{CO}_2\text{H})$. —1. *α-Oxyisovaleric* or *Isopropyl-hydroxalic acid*, $\text{H}_3\text{C}>\text{CH}-\text{HC}(\text{OH})(\text{CO}_2\text{H})$. —This acid, prepared from the corresponding bromovaleric acid, forms large tabular crystals, easily soluble in water, melting at 80°C . (176°F .), and volatilizing at about 100° . When oxidized with chromic acid mixture, it yields carbon dioxide and isobutyric acid.

The ethylic ether of this acid is formed, together with that of oxyisocaproic acid (*infra*), by the action of isopropyl iodide and zinc on ethylic oxalate, and may be obtained by evaporating the potash-solution used in the preparation of oxyisocaproic acid, acidulating with sulphuric acid, agitating with ether and evaporating the ethereal solution. The oxyisovaleric acid then remains as a thick liquid which solidifies in the exsiccator.

2. *Methyl-ethylloxalic acid*, $\text{H}_3\text{C}>\text{C}(\text{OH})(\text{CO}_2\text{H})$, obtained by the action of a mixture of methylic and ethylic iodide and zinc on ethyl oxalate, forms white crystals, easily soluble in water, and melting at 63°C . (145.4°F .). Its ethylic ether is soluble in water, boils at 165°C . (329°F .), and is converted by phosphorus trichloride into the ethylic ether of methylcrotonic acid.

Oxycaproic Acids, $\text{C}_6\text{H}_{12}\text{O}_3 = \text{C}_5\text{H}_{11}\text{C}(\text{OH})(\text{CO}_2\text{H})$. —1. *Leucic acid*, probably *α-Oxycaproic acid*, $\text{C}_5\text{H}_9-\text{CHOH}-\text{CO}_2\text{H}$, is produced by the action of nitrous acid on leucine or amidocaproic acid (see *AMIDES*). It forms needles or monoclinic prisms, soluble in water, alcohol, and ether, melting at about

73° C. (163.4° F.), and volatilizing at 100°. When heated for some time at that temperature, it gives off water, and leaves a syrupy oxide or anhydride. It forms crystallizable salts analogous to the lactates; the zinc salt crystallizes in shining scales.

2. *Diethyloxalic acid*, $(C_2H_5)_2C \begin{smallmatrix} \text{OH} \\ \text{CO}_2H \end{smallmatrix}$, formed by the action of ethyl iodide and zinc an ethylic oxalate, is crystalline, easily soluble in water and ether, melts at 74.5° C. (166.1° F.), and sublimes at about 500° C. (1220° F.). Its methylic ether boils at 165° C. (320° F.), and is converted by the action of phosphorus trichloride into methylic ethylcrotonate (p. 718). The free acid, oxidized by chromic acid mixture, yields diethyl-ketone, $CO(C_2H_5)_2$.

Oxylisoeptolo or **Amylhydroxalic Acid**, $C_7H_{14}O_3 = C_2H_5H \begin{smallmatrix} \text{OH} \\ \text{CO}_2H \end{smallmatrix}$, and **Diamyl-oxalic Acid**, $C_{11}H_{22}O_3 = C_5H_{11}H \begin{smallmatrix} \text{OH} \\ \text{CO}_2H \end{smallmatrix}$, are formed by the action of zinc and isopentyl iodide on ethylic oxalate. The former is a thick syrup; its ethylic ether boils at 203° C. (397.4° F.). The latter crystallizes in silky needles, is nearly insoluble in water, and melts at 122° C. (251.6° F.). Its ethylic ether boils at 262° C. (503.6° F.).

Oxylisocaprylic or **Di-isopropyloxalic Acid**, $C_8H_{16}O_3 = (C_3H_7)_2C \begin{smallmatrix} \text{OH} \\ \text{CO}_2H \end{smallmatrix}$, obtained by the action of isopropyl iodide and zinc on ethylic oxalate, forms slender needles, slightly soluble in water, melts at 110°–111° C. (230°–231.8° F.), and sublimes at a moderate heat.

Carbonic Acid, $CH_2O_3 = CO \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$.—This acid belongs to the lactic series, so far as its constitution is concerned, being derived from the unknown methene glycol, $CH_2 \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$, by substitution of O for H_2 ; but it differs from all the other acids of the series in being bibasic, both the hydroxyl groups contained in it being immediately connected with an atom of oxygen, so that either of the hydrogen-atoms may be regarded as belonging to the group CO_2H .

Carbonic acid itself, or hydrogen carbonate, is not known, inasmuch as when a metallic carbonate is decomposed by a stronger acid, the hydrogen carbonate, CH_2O_3 , always splits up into water and carbon dioxide, which escapes as gas. The corresponding sulphur compound, CH_2S_3 , is, however, obtained as an oily liquid when a metallic thio-carbonate is decomposed by an acid (p. 201).

With the alkali-metals carbonic acid forms acid and normal or neutral salts, according as one or both of the hydrogen-atoms are replaced; e. g.,

Acid sodium carbonate, $CHNaO_3$, or $CO \begin{smallmatrix} \text{OH} \\ \text{ONa} \end{smallmatrix}$

Normal sodium carbonate, CNa_2O_3 , or $CO(ONa)_2$.

With dyad-metals, carbonic acid forms only normal salts, $CM''O_3$, and basic salts; the so-called acid carbonates of barium, calcium, etc., are known only in solution, and are, in fact, merely solutions of neutral car-

bonates in aqueous carbonic acid, which give off carbon dioxide on boiling. The basic carbonates of dyad metals may be viewed as compounds of normal carbonates with metallic oxides or hydrates; for example, slaked lime, produced by exposing quicklime to moist air, has the composition of a dicaleic carbonate, $\text{CaO} \cdot \text{CaCO}_3 \cdot \text{Aq.}$; and native green copper carbonate, or malachite, consists of $\text{CuO} \cdot \text{CuCO}_3 + \text{H}_2\text{O}$. These basic carbonates may, however, be viewed in another way, namely, as derived from a tetratomic carbonic acid, or ortho-carbonic acid, CH_2O_4 , or $\text{C}(\text{OH})_4$, analogous to methane and carbon tetrachloride; thus, dicaleic carbonate = $(\text{Ca}_2\text{O}_4 + \text{H}_2\text{O})$; malachite = $(\text{Cu}_2\text{O}_4 + \text{H}_2\text{O})$.

With metals of higher atomicity, carbonic acid does not form definite salts.

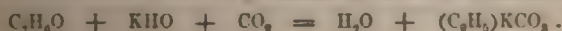
CARBONIC ETHERS.—The only carbonic ethers known are those in which the two hydrogen-atoms of carbonic acid are replaced either by two equivalents of a monad alcohol-radicle, or by one equivalent of a monad alcohol-radicle and one equivalent of metal.

Ethyl carbonate, $(\text{C}_2\text{H}_5)_2\text{CO}_3$, is formed by the action of ethyl iodide on silver carbonate:—



also by the action of potassium or sodium on ethyl oxalate, $(\text{C}_2\text{H}_5)_2\text{C}_2\text{O}_4$; this reaction is not quite understood, but it amounts to the removal of carbon monoxide, or carbonyl, CO , from the oxalic ether. Fragments of potassium or sodium are dropped into oxalic ether as long as gas is disengaged: the brown pasty product is then mixed with water and distilled. The carbonic ether is found floating upon the surface of the water of the receiver as a colorless, limpid liquid of aromatic odor and burning taste. It boils at 125°C. (257°F.), and is decomposed by an alcoholic solution of potash into potassium carbonate and alcohol. By chlorine in diffused daylight it is converted into dichlorethyl carbonate, $(\text{C}_2\text{H}_4\text{Cl})_2\text{CO}_3$, and in sunshine into pentachlorethyl carbonate, $(\text{C}_2\text{Cl}_5)_2\text{CO}_3$.

Ethyl-potassium carbonate, $(\text{C}_2\text{H}_5)_2\text{KCO}_3$, is produced by passing carbonic acid gas into a cooled solution of potassium hydroxide in absolute alcohol:



It is a white nacreous salt, decomposed by water into potassium carbonate and alcohol.

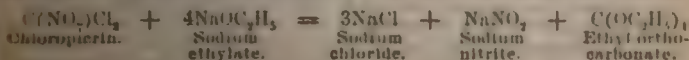
Ethyl-methyl carbonate, $(\text{C}_2\text{H}_5)(\text{CH}_3)\text{CO}_3$, is obtained by distilling a mixture of ethyl-potassium sulphate and methyl-potassium carbonate:—



Methyl-barium carbonate, $(\text{CH}_3)_2\text{Ba}(\text{CO}_3)_2$, is obtained as a white precipitate by passing carbonic acid gas into a solution of baryta in methyl alcohol.

Carbonates of *butyl*, *amyl*, and *allyl*, analogous in composition to ethyl carbonate, have also been obtained. *Phenyl-hydrogen carbonate*, or *acid phenyl carbonate*, $(\text{C}_6\text{H}_5)\text{HCO}_3$, is identical with salicylic acid, which will be described further on.

Ethyl orthocarbonate, $\text{C}(\text{OC}_2\text{H}_5)_4$, is produced by heating a mixture of chloropierin (trichloro-nitromethane) with absolute alcohol and sodium:

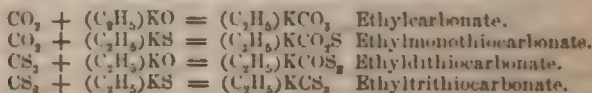


It is a colorless oil, boiling at $156^\circ\text{--}159^\circ \text{C.}$ ($316.4^\circ\text{--}318.2^\circ \text{F.}$).

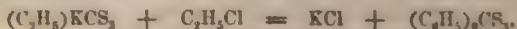
THIOCARBONIC OR SULPHOCARBONIC ETHERS.—These are bodies having the composition of carbonic ethers in which the oxygen is replaced, wholly or partly, by sulphur. The following table exhibits their names and formulae, the ethyl and ethene compounds being taken as examples :

| | |
|--|-----------------------|
| Ethyl-monothiocarbonic acid | $(C_2H_5)_H.CO_2S.$ |
| Diethyl monothiocarbonate | $(C_2H_5)_2.CO_2S.$ |
| Ethyl-dithiocarbonic or Xanthic acid | $(C_2H_5)_H.CO_2S_2.$ |
| Diethyl dithiocarbonate | $(C_2H_5)_2.CO_2S_2.$ |
| Ethyl-trithiocarbonic acid | $(C_2H_5)_H.CO_2S_3.$ |
| Diethyl trithiocarbonate | $(C_2H_5)_2.CO_2S_3.$ |
| Ethene dithiocarbonate | $(C_2H_4)_2.CO_2S_2.$ |
| Ethene trithiocarbonate | $(C_2H_4)_2.CO_2S_3.$ |

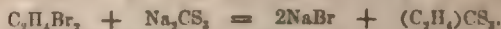
The metallic salts of the acid thiocarbonic ethers are produced in the same manner as those of the carbonic ethers: thus carbon dioxide unites with potassium sulphethylate (mercaptide), to form potassium ethylmonothiocarbonate, just as it unites with potassium ethylate to form the ethylcarbonate; and, in like manner, carbon bisulphide acts on potassium ethylate or alcoholic potash, so as to form potassium ethyldithiocarbonate; and on potassium mercaptide, or an alcoholic solution of the sulphhydrate, so as to form the ethyltrithiocarbonate, thus :



The neutral thiocarbonic ethers (containing monatomic alcohol-radicles) are produced by the action of the chlorides, bromides, etc., of alcohol-radicles on the metallic salts of the corresponding acid ethers; e. g. :



The thiocarbonic ethers of diatomic alcohol-radicles are formed by the action of diatomic alcoholic bromides, iodides, etc., on sodium thiocarbonate; e. g. :

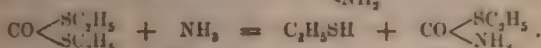


The neutral thiocarbonic ethers are oily liquids; so likewise are the acid ethers, such at least as are known in the free state, or as hydrogen salts; their metallic salts are mostly crystalline. The best known of these compounds are the ethyl-dithiocarbonates or xanthates.

To prepare xanthic acid, alcohol of 0.800 specific gravity is saturated whilst boiling, with potash, and into this solution carbon bisulphide is dropped till it ceases to be dissolved, or until the liquid loses its alkalinity. On cooling the whole to $-18^\circ C.$ ($0.4^\circ F.$), the potassium-salt separates in the form of brilliant, slender, colorless prisms, which must be quickly pressed between folds of bibulous paper, and dried in a vacuum. It is freely soluble in water and alcohol, but insoluble in ether, and is gradually destroyed by exposure to air, by oxidation of part of the sulphur. Xanthic acid may be prepared by decomposing this salt with dilute sulphuric or hydrochloric acid. It is a colorless, oily liquid, heavier than water, of powerful and peculiar odor, and very combustible: it reddens litmus paper, and ultimately bleaches it. Exposed to gentle heat (about $24^\circ C.$), it is decomposed into alcohol and carbon bisulphide. Exposed to the air, or kept beneath the surface of water open to the air, it becomes covered with a whitish crust, and is gradually destroyed. The xanthates

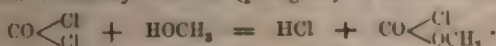
of the alkali metals and of barium are colorless and crystallizable; the calcium salt dries up to a gummy mass; the xanthates of zinc, lead, and mercury are white, and but slightly soluble; that of copper is a flocculent, insoluble substance, of beautiful yellow color.

Ethyl dithiocarbonate or *Xanthic ether*, $(C_2H_5)_2COS_2$, obtained by the action of ethyl chloride on potassium xanthate, is a pale-yellow oil, boiling at $200^\circ C.$ ($392^\circ F.$), insoluble in water, soluble in all proportions of alcohol or ether. Ammonia-gas passed into its alcoholic solution forms mercaptan and a crystalline substance, $CO<\begin{smallmatrix} SC_2H_5 \\ NH_2 \end{smallmatrix}$, called xanthamide:



Amyl dithiocarbonate, $CO(SC_5H_{11})_2$, treated in like manner, yields *amyl-xanthamide*, $CO<\begin{smallmatrix} SC_5H_{11} \\ NH_2 \end{smallmatrix}$.

Chlorocarbonic Ethers, CO_2ClR or $CO<\begin{smallmatrix} Cl \\ OR \end{smallmatrix}$, [R denoting a monatomic alcohol-radicle.]—These compounds, derived from carbonic ethers, $CO(OR)_2$, by substitution of Cl for one of the groups OR , are formed by the action of carbonyl chloride (phosgene) on the alcohols; *e. g.*:



Methyl chlorocarbonate, $CO_2Cl(CH_3)$, is a colorless mobile oil, heavier and more volatile than water, having a pungent odor, and burning with a greenish flame. Gaseous ammonia converts it into methyl carbamate (urethane):



Ethyl chlorocarbonate, $CO_2Cl(OC_2H_5)$, is also a colorless, very mobile liquid, the vapor of which is very irritating to the eyes. Specific gravity 1.139 at $13^\circ C.$ ($55.4^\circ F.$). Boiling point, $94^\circ C.$ ($201.2^\circ F.$). It is very inflammable, burns with a green flame, is decomposed by hot water, and quickly converted by ammonia into ethyl carbamate.

DIATOMIC AND TRIBASIC ACIDS.

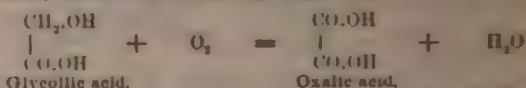
These acids contain the group, CO_2H , twice, and must therefore contain four atoms of oxygen. They may all be included in the general formula, $R''(CO_2H)_2$,— R'' denoting a diatomic hydrocarbon-radicle,—or they may be regarded as compounds of oxygenated radicles with two equivalents of hydroxyl, *e. g.*, succinic acid $= (C_4H_4O_2)''(OH)_2$.

1.—**Oxalic or Succinic Series**, $C_nH_{2n-2}O_4$, or $C_nH_{2n}<\begin{smallmatrix} CO.OH \\ CO.OH \end{smallmatrix}$.
The known acids of this series are:

| | | | |
|----------------------------|----------------|--------------------------|-------------------|
| Oxalic acid | $C_2H_2O_4$ | Pinelic acid | $C_7H_{12}O_4$ |
| Malonic acid | $C_3H_4O_4$ | Suberic acid | $C_8H_{14}O_4$ |
| Succinic acid | $C_4H_6O_4$ | Anchoic acid | $C_{10}H_{16}O_4$ |
| Prototartaric acid | $C_4H_6O_4$ | Sebacic acid | $C_{20}H_{38}O_4$ |
| Adipic acid | $C_6H_{10}O_4$ | Roccellic acid | $C_{17}H_{32}O_4$ |

They are produced:—1. By oxidation of the corresponding glycol, $R''(\text{CH}_2\text{OH})_2$, the change consisting in the substitution of O_2 for H_2 (p. 638). In this manner oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, is formed from ethene alcohol, $\text{C}_2\text{H}_4(\text{OH})_2$, and malonic acid, $\text{C}_3\text{H}_4\text{O}_4$, from 3-propene alcohol, $\text{C}_3\text{H}_6(\text{OH})_2$, but all the known glycols of higher order split up under the influence of oxidizing agents, and do not yield dibasic acids containing the same number of carbon-atoms as themselves.

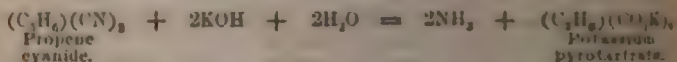
2. By oxidation of the oxyfatty acids, $\text{C}_n\text{H}_{2n}\text{O}_2$, in which the hydroxyl group is directly attached to the group $(\text{CH}_2)_2$; e. g.:



3. By boiling the cyano-derivatives of the fatty acids with alkaline acids:



4. By boiling the cyanides of diatomic alcohol-radicles with alcoholic potash; e. g.:



This reaction is analogous to that by which the fatty acids are formed from the cyanides of the monatomic alcohol-radicles, $\text{C}_n\text{H}_{2n+1}$ (p. 638).

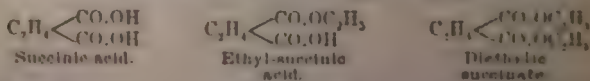
5. By the addition of hydrogen to other acids containing a smaller proportion of that element; in this manner succinic acid, $\text{C}_4\text{H}_6\text{O}_4$, is formed from fumaric acid, $\text{C}_4\text{H}_4\text{O}_4$.

6. By the action of heat on acids of more complicated structure; e. g.

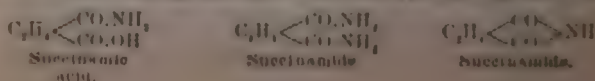


7. Many of these acids are produced by the action of powerful oxidizers on a variety of organic bodies: thus, succinic, adipic, pimelic, azelaic, and anchoic acids are produced by treating various fatty and resinous bodies with nitric acid.

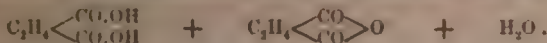
The acids of this series are solid, crystallizable, non-volatile bodies for the most part easily soluble in water, and having a strong acid reaction. Being dibasic, they form acid and neutral salts, and acid and neutral esters; thus:



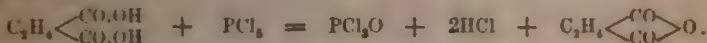
In like manner, each acid can form an acid amide or amide acid, also neutral amide or diamide by substitution of amidogen, NH_2 , for one or both of the hydroxyl groups, also a neutral imide by substitution of the bivalent-radicle imidogen, NH , for both these groups together; thus:



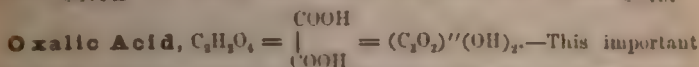
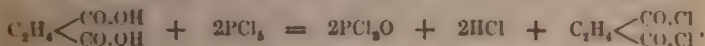
These bibasic acids, when heated, give off their water, and yield anhydrides which, when boiled with water, are reconverted into the acids :



The anhydrides are also produced by treating the acids with phosphorus pentachloride :

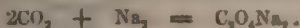


With excess of phosphorus pentachloride, acid chlorides or chloranhydrides are produced ; thus :



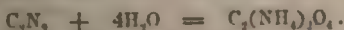
acid exists ready formed in many plants as a potassium or calcium salt, and is produced by the oxidation of a great variety of organic compounds. In some cases the reaction consists in a definite substitution of oxygen for hydrogen : thus oxalic acid is formed from ethene alcohol, $C_2H_4O_2$, by substitution of O_2 for H_2 , and from ethyl alcohol, C_2H_5O , by the same substitution and further addition of one atom of oxygen. But in most cases the reaction is more complex, consisting in a complete breaking up of the molecule. In this manner oxalic acid is produced in great abundance from more highly carbonized organic substances, such as sugar, starch, cellulose, etc., by the action of nitric acid, or by fusion with caustic alkalis.

Oxalic acid is also produced : a. As a sodium or potassium salt by direct combination of the alkali-metal with carbon dioxide :

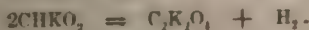


The sodium salt is obtained by passing carbon dioxide over a heated mixture of sodium and sand ; the potassium-salt by heating potassium-amalgam in the gas.*

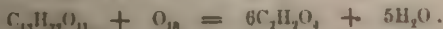
b. As an ammonium salt, together with other products, in the decomposition of cyanogen by water :



γ. As a potassium salt by heating potassium formate with excess of potash :



Preparation.—1. By the oxidation of sugar with nitric acid :

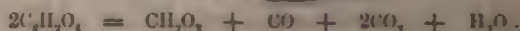


One part of sugar is gently heated in a retort with 5 parts of nitric acid of sp. gr. 1.42, diluted with twice its weight of water : copious red fumes are then disengaged, and the oxidation of the sugar proceeds with violence and rapidity. When the action slackens, heat may be again applied to the vessel, and the liquid concentrated by distilling off the superfluous nitric acid, until it deposits crystals on cooling. These are drained, redissolved in a small quantity of hot water, and the solution is set aside to cool.

* Kolbe and Drechsel, Chem. Soc. Journal [2], vi. 121.

2. By heating sawdust with caustic alkali. Many years ago, Gay-Lussac observed that wood and several other organic substances were converted into oxalic acid by fusion with caustic potash. Upon this observation, Messrs. Roberts, Dale & Co. have founded a method for the preparation of oxalic acid, which furnishes this acid at a much cheaper rate than any other process. A mixed solution of the hydrates of sodium and potassium, in the proportion of two molecules of the former to one of the latter, is evaporated to about 1.35 sp. gr., and then mixed with sawdust, so as to form a thick paste, which is placed in thin layers on iron plates. The mixture is now gradually heated, care being taken to keep it constantly stirred. The action of heat expels a quantity of water, and the mass tumescens strongly, with disengagement of much inflammable gas, consisting of hydrogen and carburetted hydrogen. The mixture is now kept for some hours at a temperature of 204° C. (400° F.), care being taken to avoid clarring, which would cause a loss of oxalic acid. The product thus obtained is a gray powder; it is now treated with water at about 15.50° C. (60° F.), which leaves the sodium oxalate undissolved. The supernatant liquid is drawn off, evaporated to dryness, and heated in furnaces to recover the alkalis, which are caustified and used for a new operation. The sodium oxalate is washed and decomposed by boiling with slaked lime, and the resulting calcium oxalate is decomposed by means of sulphuric acid. The liquid decanted from the calcium sulphate is evaporated to crystallization in leaden vessels, and the crystals are purified by re-crystallization.

Oxalic acid separates from a hot solution in colorless, transparent crystals derived from an oblique rhombic prism, and consisting of $C_2H_2O_4 \cdot 2H_2O$. The two molecules of crystallization-water may be expelled by a very gentle heat, the crystals crumbling down to a soft white powder, consisting of anhydrous oxalic acid, $C_2H_2O_4$, which may be sublimed in great measure without decomposition. The crystallized acid, on the contrary, is decomposed by a high temperature into formic acid, carbon monoxide, and carbon dioxide, without leaving any solid residue:

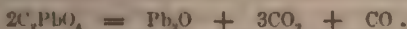


The crystals of oxalic acid dissolve in 8 parts of water at 15.50° , and in their own weight, or less, of hot water: they are also soluble in spirit. The aqueous solution has an intensely sour taste and most powerful acid reaction, and is highly poisonous. The proper antidote is chalk or magnesia. Oxalic acid is decomposed by hot oil of vitriol into a mixture of carbon monoxide and carbon dioxide: it is slowly converted into carbonic acid by nitric acid, whence arises a considerable loss in the process of manufacture from sugar. The dioxides of lead and manganese effect the same change, becoming reduced to monoxides, which form salts with the unaltered acid.

Oxalates.—Oxalic acid, like other bibasic acids, forms with monatomic metals, neutral or normal salts containing $C_2M_2O_4$, and acid salts, $C_2HM_2O_4$. With potassium and ammonium it likewise forms hyper-acid salts, e.g., C_2HKO_4 , $C_2NH_4O_4$, or $C_2H_2KO_6$. With most diatomic metals it forms only neutral salts, $C_2M'O_4$; with barium and strontium, however, it forms salts analogous to the hyper-acid oxalates of the alkali-metals. It also forms numerous well-crystallized double salts. It is one of the strongest acids, decomposing dry sodium chloride when heated, with evolution of hydrochloric acid, and converting sodium chloride or nitrate in aqueous solution into acid oxalate.

The oxalates of the alkali-metals are soluble in water: the rest are, for the most part, insoluble in water, but soluble in dilute acids.

All oxalates are decomposed by heat. The oxalates of the alkali-metals and also of the alkaline earth metals, if not too strongly heated, give off carbon monoxide and leave carbonates, while the oxalates of those metals whose carbonates are decomposed by heat (zinc and magnesium, for example), give off carbon monoxide and carbon dioxide, and leave metallic oxides. The oxalates of the more easily reducible metals (silver and copper, etc.), give off carbon dioxide and leave the metal; the lead salt leaves suboxide of lead, and gives off 3 volumes of carbon dioxide to 1 volume of carbon monoxide:—



Oxalates heated with *sulphuric acid* give off carbon monoxide and dioxide, and leave a residue of sulphate. In this case, as well as in the decomposition by heat alone, no separation of carbon takes place, and consequently the residue does not blacken: this character distinguishes the oxalates from the salts of all other carbon acids.

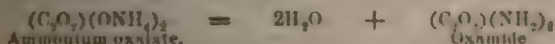
Oxalic acid and the soluble oxalates give with *calcium chloride* a precipitate of calcium oxalate, insoluble in water and in acetic acid, but soluble in hydrochloric and nitric acid. This reaction affords a very delicate test for the presence of oxalic acid: the insolubility of the precipitated oxalate in acetic acid distinguishes it at once from the phosphate.

POTASSIUM OXALATE.—The *neutral salt*, $\text{C}_2\text{K}_2\text{O}_4 \cdot 2\text{Aq.}$, prepared by neutralizing oxalic acid with potassium carbonate, crystallizes in transparent rhombic prisms, which become opaque and anhydrous by heat, and dissolve in 3 parts of water.—The *acid oxalate* or *binoxalate*, $\text{C}_2\text{HKO}_4 \cdot 2\text{Aq.}$, sometimes called *Salt of Sorrel*, from its occurrence in that plant, is found also in other species of *Rumex*, in *Oxalis acetosella*, and in garden rhubarb, associated with malic acid. It is easily prepared by dividing a solution of oxalic acid in hot water into two equal portions, neutralizing one with potassium carbonate, and adding the other: the salt crystallizes, on cooling, in colorless rhombic prisms. The crystals have a sour taste, and require 40 parts of cold, and 6 of boiling water for solution. A solution of this salt is often used for removing ink from paper. The *hyper-acid oxalate* or *quadroxalate*, $\text{C}_2\text{KH}_3\text{O}_4 \cdot 2\text{Aq.}$, is prepared by saturating 1 part of oxalic acid with potassium carbonate, and adding 3 parts of oxalic acid. The crystals are triclinic, and dissolve in 20 parts of water at 20°C . (68°F.).

Sodium oxalate, $\text{C}_2\text{Na}_2\text{O}_4$, is slightly soluble and difficult to crystallize. The *acid salt*, C_2HNaO_4 , forms crystals which redden litmus.

AMMONIUM OXALATES.—The *neutral salt*, $\text{C}_2(\text{NH}_4)_2\text{O}_4 + 2\text{Aq.}$, is prepared by neutralizing a hot solution of oxalic acid with ammonium carbonate. It crystallizes in long, colorless, rhombic prisms, which effloresce in dry air. They are not very soluble in cold water, but dissolve freely with the aid of heat.

The dry salt, when heated in a retort, gives off water, and yields a sublimate of oxamide.*



When distilled with phosphoric oxide, it gives up four molecules of

* See the Chapter on Amides.

2. By heating sawdust with caustic alkali. Many years ago, $C_2(NH_2)_2O$,—observed that wood and several other organic substances, at the same time, into oxalic acid by fusion with caustic potash.

Messrs. Roberts, Dale & Co. have founded a method of preparing oxalic acid, $C_2O_4 + Ag_2O$, is still one of the best processes. A mixed solution of the two acids yields oxamic acid in the proportion of two molecules of oxamic acid to one of oxalic acid.

evaporated to about 1.35 sp. gr., and form a thick paste, which is plb. This salt occurs in the juice of several plants at the end of the growing season in great quantities.

It is also a frequent constituent of animal fluids, and whenever oxalic acid or an oxalate is present, it falls as a white powder, which requires some hours at a temperature of 15.50° C. (60° F.) to avoid clarring, which is a little soluble in dilute hydrochloric acid.

Nitric acid dissolves it easily. When dried in a vacuum, it may be driven off by exposure to a red heat in a close vessel, it is a white powder, which requires some hours at a temperature of 15.50° C. (60° F.) to avoid clarring, which is a little soluble in dilute hydrochloric acid.

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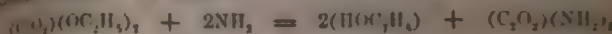
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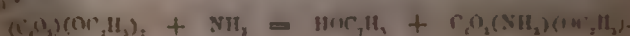
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This is the best process for preparing oxamide.

When dry gaseous ammonia is conducted into a vessel containing sawdust, the gas is rapidly absorbed, and a white solid substance is produced, which is soluble in hot alcohol, and separates on cooling in transparent, transparent, acaly crystals. They dissolve in water, and are both fusible and volatile. This substance is oxamethane, the ethylic ether of oxamic acid.



* See the Chapter on Amides.

formed when ammonia in small quantity is added to the ether in alcohol.

When treated with excess of dry chlorine in sunshine, a white, fine, fusible body is produced, insoluble in water, and soluble by alcohol. It consists of perchlorethylic ether, $(C_2Cl_3)_2C_2O_4$, or oxalic ether in which the whole of the hydrogen is replaced by chlorine.

It is converted by potassium or sodium into ethyl carbonate, and carbon monoxide: $C_2(C_2H_5)_2O_4 = C(C_2H_5)_2O_3 + CO$; but the reaction is complicated by the formation of several other products.

When ethyl oxalate is agitated with sodium amalgam in a vessel exposed to the air, a product is obtained which is separated by ether into a soluble and an insoluble portion, the latter consisting of fermentable sugar, and the former of sodium oxalate, and at least one other sodium-salt, while the soluble portion yields, by spontaneous evaporation, crystals having the composition $C_{11}H_{18}O_8$, and consisting of the ethylic ether of a tribasic acid, called deoxalic acid, because it is produced by deoxidation of oxalic acid: $5C_2H_2O_4 + 5H_2 = 2C_3H_4O_6 + 4H_2O$; and racemocarbonic acid, because it contains the elements of racemic acid, $C_4H_4O_6$, and carbon monoxide, CO , and is resolved into these two compounds when its aqueous solution is heated in a sealed tube with a small quantity of sulphuric acid. The decomposition of ethylic oxalate by sodium amalgam has not been completely investigated, but the formation of deoxalic acid and glucose may be represented by the equation:



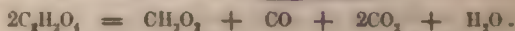
Ethyl oxalate, treated with zinc-ethyl, and afterwards with water, yields the ethylic ether of diethoxalic acid, $C_2H_5(C_2H_5)_2O_4$, and similar products with zinc-methyl and zinc-amyl (p. 714).

Acid ethyl oxalate, or Ethyloxalic acid, $C_2H(C_2H_5)O_4$, or $C_2O_2 \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OH} \end{smallmatrix}$, is obtained as a potassium-salt by adding to a solution of neutral ethyl oxalate in absolute alcohol, a quantity of alcoholic potash less than sufficient to convert the whole into potassium oxalate and alcohol; on dissolving this salt in hydrated alcohol, carefully saturating with sulphuric acid, and neutralizing with carbonate of lead or barium, the ethyloxalate of lead or barium is obtained.—The acid itself is prepared by decomposing either of these salts with sulphuric acid; but it is very unstable, and is decomposed by concentration into alcohol and oxalic acid. The potassium salt, $C_2O_2 \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OK} \end{smallmatrix}$, forms crystalline scales, which begin to decompose towards 100°.

METHYL OXALATE, $C_2(CH_3)_2O_4$, or $C_2O_2(OCH_3)_2$, is easily prepared by distilling a mixture of equal weights of oxalic acid, wood-spirit, and oil of vitriol. A spiritous liquid collects in the receiver, which, when exposed to the air, quickly evaporates, leaving the methyl oxalate in the form of transparent, transparent, crystalline plates, which may be purified by pressure between folds of bibulous paper, and redistilled from a little oxide of lead. The product is colorless, and has the odor of ethyl oxalate; it melts at 54° C. (128.8° F.), and boils at 161° C. (321.8° F.); dissolves freely in alcohol and wood-spirit, also in water, which, however, rapidly decomposes it, especially when hot, into oxalic acid and wood-spirit. The alkaline hydrates effect the same change even more easily. Solution of ammonia converts it into oxamide and methyl alcohol. With dry ammoniacal gas

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Oxalic acid separates from a hot solution in colorless, transparent crystals derived from an oblique rhombic prism, and consisting of $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The two molecules of crystallization-water may be expelled by a very gentle heat, the crystals crumbling down to a soft white powder, consisting of anhydrous oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, which may be sublimed in great measure without decomposition. The crystallized acid, on the contrary, is decomposed by a high temperature into formic acid, carbon monoxide, and carbon dioxide, without leaving any solid residue:



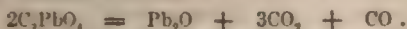
The crystals of oxalic acid dissolve in 8 parts of water at 15.5° , and in their own weight, or less, of hot water: they are also soluble in spirit. The aqueous solution has an intensely sour taste and most powerful acid reaction, and is highly poisonous. The proper antidote is chalk or magnesia. Oxalic acid is decomposed by hot oil of vitriol into a mixture of carbon monoxide and carbon dioxide: it is slowly converted into carbonic acid by nitric acid, whence arises a considerable loss in the process of manufacture from sugar. The dioxides of lead and manganese effect the same change, becoming reduced to monoxides, which form salts with the unaltered acid.

Oxalates.—Oxalic acid, like other bibasic acids, forms with monatomic metals, neutral or normal salts containing $\text{C}_2\text{M}_2\text{O}_4$, and acid salts, $\text{C}_2\text{HM}_2\text{O}_4$. With potassium and ammonium it likewise forms hyper-acid salts, e.g. C_2HKO_4 , $\text{C}_2\text{H}_2\text{O}_4$, or $\text{C}_2\text{H}_3\text{KO}_4$. With most diatomic metals it forms only neutral salts, $\text{C}_2\text{M}'\text{O}_4$; with barium and strontium, however, it forms acid salts analogous to the hyper-acid oxalates of the alkali-metals. It also forms numerous well-crystallized double salts. It is one of the strongest acids, decomposing dry sodium chloride when heated, with evolution of hydrochloric acid, and converting sodium chloride or nitrate in aqueous solution into acid oxalate.

Oxalates of the alkali-metals are soluble in water; the rest are, for the most part, insoluble in water, but soluble in dilute acids.

Oxalates are decomposed by heat. The oxalates of the alkali-metals and of the alkaline earth metals, if not too strongly heated, give off carbon monoxide and leave carbonates, while the oxalates of those metals whose carbonates are decomposed by heat (zinc and magnesium, for example), give off carbon monoxide and carbon dioxide, and leave metallic

The oxalates of the more easily reducible metals (silver and copper, etc.), give off carbon dioxide and leave the metal; the lead salt gives sub-oxide of lead, and gives off 3 volumes of carbon dioxide to 1 volume of carbon monoxide:—



Oxalates heated with *sulphuric acid* give off carbon monoxide and dioxide and leave a residue of sulphate. In this case, as well as in the decomposition by heat alone, no separation of carbon takes place, and constantly the residue does not blacken: this character distinguishes the oxalates from the salts of all other carbon acids.

Oxalic acid and the soluble oxalates give with *calcium chloride* a precipitate of calcium oxalate, insoluble in water and in acetic acid, but soluble in hydrochloric and nitric acid. This reaction affords a very delicate test for the presence of oxalic acid: the insolubility of the precipitated oxalate in acetic acid distinguishes it at once from the phosphate.

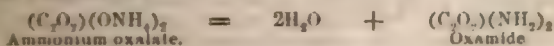
POTASSIUM OXALATES.—The *neutral salt*, $\text{C}_2\text{K}_2\text{O}_4 \cdot 2\text{Aq.}$, prepared by neutralizing oxalic acid with potassium carbonate, crystallizes in transparent rhombic prisms, which become opaque and anhydrous by heat, and dissolve in 3 parts of water.—The *acid oxalate* or *bi-oxalate*, $\text{C}_2\text{HKO}_4 \cdot 2\text{Aq.}$, known as *Salt of Sorrel*, from its occurrence in that plant, is found in other species of *Rumex*, in *Oxalis acetosella*, and in garden rhubarb, saturated with malic acid. It is easily prepared by dividing a solution of oxalic acid in hot water into two equal portions, neutralizing one with potassium carbonate, and adding the other: the salt crystallizes, on cooling, in colorless rhombic prisms. The crystals have a sour taste, and require 40 parts of cold, and 6 of boiling water for solution. A solution of this salt is often used for removing ink from paper. The *hyper-acid oxalate* or *quadr-oxalate*, $\text{C}_2\text{KH}_3\text{O}_4 \cdot 2\text{Aq.}$, is prepared by saturating 1 volume of oxalic acid with potassium carbonate, and adding 3 parts of oxalic acid.

The crystals are triclinic, and dissolve in 20 parts of water at 20°C (68°F.).

Sodium oxalate, $\text{C}_2\text{Na}_2\text{O}_4$, is slightly soluble and difficult to crystallize. *Sodium acid salt*, C_2HNaO_4 , forms crystals which redden litmus.

AMMONIUM OXALATES.—The *neutral salt*, $\text{C}_2(\text{NH}_4)_2\text{O}_4 + 2\text{Aq.}$, is prepared by neutralizing a hot solution of oxalic acid with ammonium carbonate. It crystallizes in long, colorless, rhombic prisms, which effloresce in dry air. They are not very soluble in cold water, but dissolve freely with the aid of heat.

The dry salt, when heated in a retort, gives off water, and yields a substance of oxamide:*



When distilled with phosphoric oxide, it gives up four molecules of

* See the Chapter on Amides.

water, and yields a on $4\text{H}_2\text{O} = 2\text{CN}$. Other.

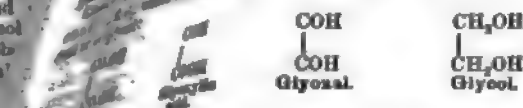
Acid oxonium of soluble than the (239.80 F.), it has $\text{C}_2\text{H}_2\text{NO}_2$ or (C_2O_2) .

CALCIUM OXAL plants, and some scopic octahedral deposits and added to a sol density by b quite insol at 1000, it rather high converted

The ox oxalate, soluble + 3Ag inste. acid, by red blue been

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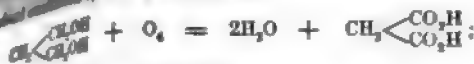
DIATOMIC AND DIATOMIC ACIDS
A white crystalline or amorphous $\text{CO} \angle \text{OCH}_3$, a white crystalline substance has melted to purely cubes.
Some think, COCH_3 or $(\text{CO}(\text{C}_2\text{H}_5\text{O}_2)) = \text{C}_2\text{O}_2 \angle \text{OCH}$
Some are formed by the action of silver bromide on silver oxalate, which is white and is glyoxylic acid, $\text{C}_2\text{H}_2\text{O}_3$, and which may be regarded as aldehydic derivatives of



and are formed in diatomic products in the oxidation of glycol or converted by further oxidation into oxalic acid (see ALDEHYDES).

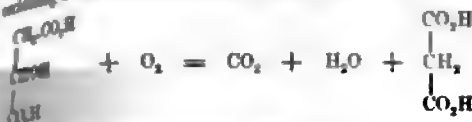
Malonic Acid, $\text{C}_3\text{H}_4\text{O}_4 = \text{CH}_2 \angle \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$ —This acid is formed

by oxidation of 4-propene glycol:



also by oxidation of propene and allylene.

2. By oxidizing malic acid with chromic acid mixture:



2. By decomposition of barbituric acid (Malonyl-urea: see AMIDES).

4. Synthetically by the action of alkalis on cyanacetic acid, better the only by ether:



Ethyl monochloracetate is heated with solution of potassium cyan and the product is boiled with potash as long as it continues to give ammonia. The alkaline solution is then acidulated with sulphuric acid and the free malonic acid extracted by ether.

Malonic acid crystallizes in large rhombohedral plates; dissolves in water, alcohol, and ether; melts at 132°C . (269.6°F .); and decomposes at a higher temperature into acetic acid and carbon dioxide. Calcium salt, $\text{C}_3\text{H}_2\text{BaO}_6 + \text{H}_2\text{O}$, forms silky needles. The calcium $\text{C}_3\text{H}_2\text{CaO}_6 + 7\text{H}_2\text{O}$, is very slightly soluble in cold water.

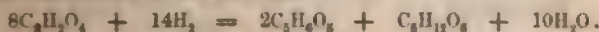
Nitrosomalonic Acid, $\text{CH}(\text{NO}) \angle \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$, formed by heating tartaric acid (p. r.) with alkalis, crystallizes in shining needles, easily soluble in water. When heated it melts, and then explodes.

The same substance is formed when ammonia in small quantity is added to a solution of oxalic ether in alcohol.

When oxalic ether is treated with excess of dry chlorine in sunshine, a white, colorless, crystalline, fusible body is produced, insoluble in water, and instantly decomposed by alcohol. It consists of perchlorethylic oxalate, $C_2Cl_6O_4$, or $(C_2Cl_5)_2O_4$, or oxalic ether in which the whole of the hydrogen is replaced by chlorine.

Ethyl oxalate is converted by potassium or sodium into ethyl carbonate, with evolution of carbon monoxide: $C_2(C_2H_5)_2O_4 = C(C_2H_5)_2O_2 + CO$; but the reaction is complicated by the formation of several other products.

When ethyl oxalate is agitated with sodium amalgam in a vessel externally cooled, a product is obtained which is separated by ether into a soluble and an insoluble portion, the latter consisting of fermentable sugar, together with sodium oxalate, and at least one other sodium-salt, while the ethereal solution yields, by spontaneous evaporation, crystals having the composition $C_{11}H_{16}O_8$, and consisting of the ethylic ether of a tribasic acid, H_3O_8 , called deoxalic acid, because it is produced by deoxidation of gallic acid: $5C_3H_2O_4 + 5H_2 = 2C_3H_6O_8 + 4H_2O$; and racemocarbonic acid, because it contains the elements of racemic acid, $C_3H_6O_8$, and carbon oxide, CO_2 , and is resolved into these two compounds when its aqueous solution is heated in a sealed tube with a small quantity of sulphuric acid. The decomposition of ethylic oxalate by sodium amalgam has not been completely investigated, but the formation of deoxalic acid and glucose may be represented by the equation:



Ethyl oxalate, treated with zinc-ethyl, and afterwards with water, yields the ethylic ether of diethoxalic acid, $C_2H_2(C_2H_5)_2O_8$, and similar products with zinc-methyl and zinc-amyl (p. 714).

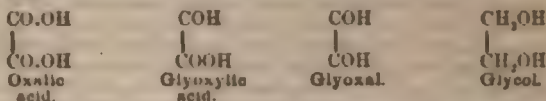
Acid ethyl oxalate, or Ethyloxalic acid, $C_2H(C_2H_5)O_6$, or $C_2O_2 \begin{smallmatrix} OC_2H_5 \\ OH \end{smallmatrix}$, is obtained as a potassium-salt by adding to a solution of neutral ethyl oxalate in absolute alcohol, a quantity of alcoholic potash less than sufficient to convert the whole into potassium oxalate and alcohol; on dissolving this salt in hydrated alcohol, carefully saturating with sulphuric acid, and neutralizing with carbonate of lead or barium, the ethyloxalate of lead or barium is obtained.—The acid itself is prepared by decomposing either of these salts with sulphuric acid; but it is very unstable, and is decomposed by concentration into alcohol and oxalic acid. The potassium salt, $C_2O_2 \begin{smallmatrix} OC_2H_5 \\ K \end{smallmatrix}$, forms crystalline scales, which begin to decompose towards 100°.

METHYL OXALATE, $C_2(CH_3)_2O_4$, or $C_2O_2(OCH_3)_2$, is easily prepared by distilling a mixture of equal weights of oxalic acid, wood-spirit, and oil of vitriol. A spiritous liquid collects in the receiver, which, when exposed to the air, quickly evaporates, leaving the methyl oxalate in the form of rhombic, transparent, crystalline plates, which may be purified by pressure between folds of bibulous paper, and redistilled from a little oxide of lead. The product is colorless, and has the odor of ethyl oxalate; it melts at 51° C. (128.8° F.), and boils at 161° C. (321.8° F.); dissolves freely in alcohol and wood-spirit, also in water, which, however, rapidly decomposes it, especially when hot, into oxalic acid and wood-spirit. The alkaline hydrates effect the same change even more easily. Solution of ammonia converts it into oxamide and methyl alcohol. With dry ammoniacal gas

it yields methyl oxamate, or oxamethylene, $C_7O_7 \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{OCH}_3 \end{smallmatrix}$, a white, solid substance, which crystallizes from alcohol in pearly cubes.

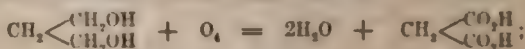
ETHENE OXALATE, $C_2O_4(C_2H_2)$, or $(C_2O_2)(C_2H_2O_2) = C_7O_7 \begin{smallmatrix} \text{OCH}_2 \\ \diagup \\ \text{NH}_2 \end{smallmatrix}$, appears to be formed by the action of ethene bromide on silver oxalate.

Closely related to oxalic acid are glyoxylic acid, $C_2H_2O_3$, and glyoxal, $C_2H_2O_2$, which may be regarded as aldehydic derivatives of oxalic acid or of glycol:



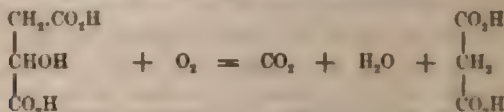
Both are formed as intermediate products in the oxidation of glycol, and are converted by further oxidation into oxalic acid (see ALDEHYDES, p. 673).

Malonic Acid, $C_3H_4O_4 = CH_2 \begin{smallmatrix} \text{CO}_2\text{H} \\ \diagup \\ \text{CO}_2\text{H} \end{smallmatrix}$.—This acid is formed: 1. By gradual oxidation of 2-propene glycol:



also by oxidation of propene and allylene.

2. By oxidizing malic acid with chromic acid mixture:



3. By decomposition of barbituric acid (Malonyl-urea: see AMIDES).

4. Synthetically by the action of alkalis on cyanacetic acid, better, on its ethylic ether:



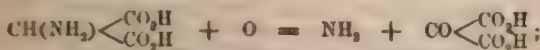
Ethylic mono-chloroacetate is heated with solution of potassium cyanide and the product is boiled with potash as long as it continues to give off ammonia. The alkaline solution is then acidulated with sulphuric acid, and the free malonic acid extracted by ether.

Malonic acid crystallizes in large rhombohedral plates; dissolves easily in water, alcohol, and ether; melts at 132°C . (269.6°F .); and decomposes at a higher temperature into acetic acid and carbon dioxide. Its barium salt, $C_3H_2\text{BaO}_4 + H_2O$, forms silky needles. The calcium salt, $4C_3H_2\text{CaO}_4 + 7H_2O$, is very slightly soluble in cold water.

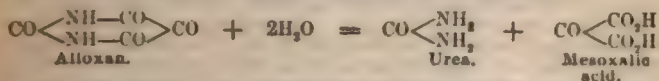
Nitrosomalonic Acid, $CH(\text{NO}) \begin{smallmatrix} \text{CO}_2\text{H} \\ \diagup \\ \text{CO}_2\text{H} \end{smallmatrix}$, formed by heating violuric acid (q. v.) with alkalis, crystallizes in shining needles, easily soluble in water. When heated it melts, and then explodes.

Amidomalonic Acid, $\text{CH}(\text{NH}_2) \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$, produced by the action of sodium-amalgam on the nitroso-acid, forms shining prisms, which, when heated, are resolved into carbon dioxide and amidacetic acid, $\text{CH}_2(\text{NH}_2)-\text{CO}_2\text{H}$.

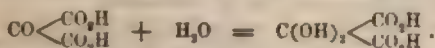
Mesoxalic Acid, $\text{C}_3\text{H}_2\text{O}_5 = \text{CO} \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$.—This ketonic acid, derived from malonic acid by substitution of O for H_2 in the group CH_2 , is produced by oxidizing amidomalonic acid by means of iodine in an aqueous solution containing potassium iodide:



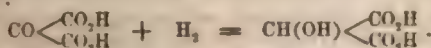
also by boiling alloxan (mesoxalyl-urea *q. v.*) with alkalis:



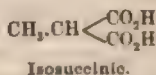
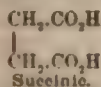
Mesoxalic acid crystallizes in deliquescent prisms, containing 1 mol. water, easily soluble in alcohol and ether. It melts at 115°C . (239°F .) without giving off its water of crystallization, and decomposes at a higher temperature. The water appears therefore to be very intimately combined, probably in the form represented on the right-hand side of the following equation:



The metallic mesoxalates and the ethylic ether also contain 1 mol. water very intimately combined; the ether probably has the constitution $\text{C}(\text{OH})_2(\text{CO}_2\text{C}_2\text{H}_5)_2$. The barium salt, $\text{C}_3\text{BaO}_5 + 1\frac{1}{2}\text{H}_2\text{O}$, is nearly insoluble in water. The silver salt, $\text{C}_3\text{Ag}_2\text{O}_5 + \text{H}_2\text{O}$, is an amorphous powder, which blackens on exposure to light, and is decomposed by boiling with water into mesoxalic acid, metallic silver, silver oxalate, and carbon dioxide. By the action of sodium-amalgam mesoxalic acid is converted into tartronic acid:



Succinic Acids, $\text{C}_4\text{H}_4\text{O}_4 = \text{C}_2\text{H}_2 \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$.—Of these acids there are two modifications, viz.:

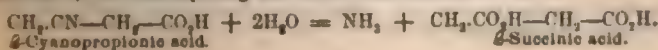


1. **Ordinary Succinic, β -Succinic, or Ethene-dicarboxylic Acid**, is produced:

1. By heating ethene cyanide with alcoholic potash:



2. By converting β iodopropionic acid into the corresponding cyanogen derivative, and decomposing the latter with alkalis or acids:



3. By the action of nascent hydrogen (evolved by sodium-amalgam) on maleic acid, or its isomeride, fumaric acid: $C_4H_2O_4 + H_2 = C_4H_4O_4$.

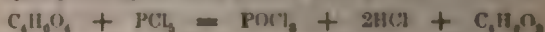
4. By the action of hydriodic acid (or water and phosphorus) on maleic acid, $C_4H_2O_4$, or tartaric acid, $C_4H_4O_6$, the reaction consisting in the abstraction of 1 or 2 atoms of oxygen, with formation of water and separation of iodine.

5. By the fermentation of maleic or fumaric acid, and of many other organic substances, especially under the influence of putrefying cases (a small quantity also during the alcoholic fermentation of sugar (p. 561 foot-note)).

6. By the oxidation of many organic substances, especially of the butyric acids, $C_4H_8O_2$, and their glycerides, under the influence of nitric acid. The formation from butyric acid is represented by the equation $C_4H_8O_2 + O = H_2O + C_4H_4O_4$.

Succinic acid occurs readily formed in amber and in certain limestones, and occasionally in the animal organism. By heating amber in iron retorts it may be obtained in colored crystals, which may be purified by treatment with nitric acid and recrystallization from boiling water. It is, however, more advantageously prepared by the fermentation of maleic acid, the crude calcium malate obtained by neutralizing the juice of mountain-ash berries with chalk or slaked lime being used for the purpose. The salt is mixed in an earthen jar with water and yeast, or decaying cheese, and left for a few days at 30° or 40° C. (86°–104° F.), the calcium succinate thus obtained is decomposed by dilute sulphuric acid; and the succinic acid is purified by crystallization from water and by sublimation.

Succinic acid crystallizes in colorless, monoclinic prisms, which dissolve in 23 parts of water at 20° C. (68° F.), and in 4 parts of boiling water; it melts at 180° C. (356° F.), and boils at 235° C. (455° F.), at the same time undergoing decomposition into water and succinic oxide or anhydride, $C_4H_2O_3$, or $(C_4H_2O_3)_2$. The same compound is formed by the action of phosphorus pentachloride on succinic acid:



It is a white mass, less soluble in water, but more soluble in alcohol, than succinic acid.

Succinic acid, being bibasic, forms, with monad metals, acid and neutral salts, $C_4H_2MO_4$ and $C_4H_4M_2O_4$, and with dyad metals, neutral salts containing $C_4H_4M''O_4$, and acid salts $C_4H_2M''O_4$, $C_4H_4O_6$.—There are also a few double succinates, several basic lead-salts, and a hyperacid potassium-salt.

The succinates of the alkali-metals are easily soluble in water. The calcium-salt, $C_4H_4CaO_4$, is sparingly soluble in water, and separates from a cold solution with $3H_2O$, and from a hot solution with H_2O . On adding ammonium succinate to the solution of a ferric salt, a basic ferric succinate is thrown down as a reddish-brown precipitate.

Succinic acid is distinguished from benzole acid by not being precipitated from its soluble salts by mineral acids, and by forming a white precipitate with baryum chloride, on addition of alcohol and ammonia.

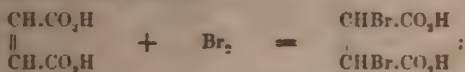
Ethyl succinate, $C_4H_4(CO_2C_2H_5)_2$, obtained by the action of hydrochloric acid on an alcoholic solution of succinic acid, is a thick oil, miscible with water, having a specific gravity of 1.072 at 0°, and boiling at 245° (420.8° F.).

Succinic chloride, $C_4H_2(CO_2Cl)_2$, formed by the action of PCl_5 on excess of succinic acid, is an oil which solidifies at 0°, and boils at 90° C. (194° F.).

Bromo-succinate acids.—The mono- and di-brominated acids are formed by heating succinic acid with bromine and water in sealed tubes at 150°–180° C. (302°–346° F.).

Monobromosuccinic acid, $C_4H_5Br(CO_2H)_2$, which is the chief product formed when a large quantity of water is used, crystallizes in nodular groups of slender needles, easily soluble in water. It melts at $160^\circ C.$ ($320^\circ F.$), giving off HBr , and being converted into fumaric acid, $C_4H_4O_4$. By boiling with silver oxide and water, it is converted into oxy succinic or maleic acid, $C_4H_3(OH)(CO_2H)_2$.

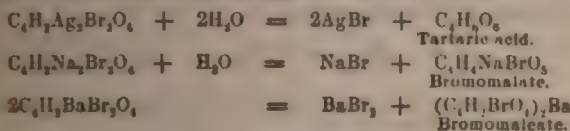
Dibromosuccinic acid, $C_4H_2Br_2(CO_2H)_2$, is also formed by direct combination of fumaric acid with bromine:



further by heating succinyl chloride with bromine, and decomposing the resulting dibromosuccinyl chloride, $C_4H_2Br_2(COCl)_2$, with water.

This acid crystallizes in prisms, sparingly soluble in cold, more freely in hot water.

Its salts are decomposed by boiling with water, the silver salt yielding dioxysuccinic or inactive tartaric acid; the sodium salt, monobromomaleic acid, and the barium salt, monobromomaleic acid; thus:



Fehlyic dibromosuccinate, $C_4H_2Br_2(CO_2C_2H_5)_2$, melts at $58^\circ C.$ ($136.4^\circ F.$), and boils at $140^\circ-150^\circ C.$ ($284^\circ-302^\circ F.$).

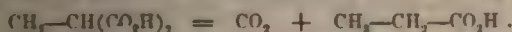
Sulphosuccinic acid, $C_4H_3(SO_3H)(CO_2H)_2$, is a tribasic acid formed by dissolving succinic acid in fuming sulphuric acid, and by the combination of fumaric or maleic acid with the acid sulphites of the alkali-metals.

Isosuccinic or Ethidene-dicarbonic Acid, $H_2C=CH\begin{smallmatrix} CO_2H \\ \diagdown \\ CO_2H \end{smallmatrix}$, is prepared from α -chloropropionic acid, through the medium of the cyanogen-derivative:—



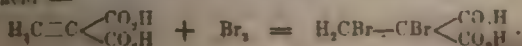
It cannot be prepared from ethidene dibromide, $H_2C=CHBr_2$; for on heating this compound with potassium cyanide and an alkali, a molecular transposition takes place, resulting in the formation of ordinary or ethenesuccinic acid.

Isosuccinic acid crystallizes in needles soluble in 4 parts of water. It melts at $130^\circ C.$ ($266^\circ F.$), and is resolved at higher temperatures into propionic acid and carbon dioxide:—



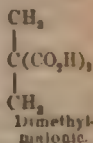
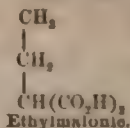
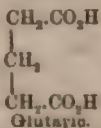
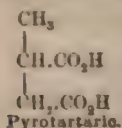
The same decomposition takes place on heating the acid with water above 100° ; in fact, this mode of decomposition into CO_2 and a monocarbon acid is characteristic of the dicarbon acids in which the two carboxyl groups are attached to one carbon-atom.

Dibromoisosuccinic acid, $C_4H_2Br_2(CO_2H)_2$, is formed by addition of bromine to maleic acid:—



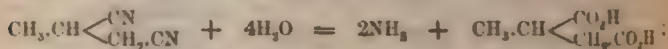
It is crystalline, easily soluble in water, melts at 150°C . (302°F .), and is resolved on further heating, or on boiling with water, into HBr , and α -bromomaleic acid, $\text{CHBr}=\text{C}(\text{CO}_2\text{H})_2$. Sodium amalgam converts it, by molecular transposition, into ordinary succinic acid.

Pyrotartaric Acids, $\text{C}_5\text{H}_6\text{O}_4 = \text{C}_5\text{H}_6\left\langle \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix} \right.$ —Of these acids there are four modifications:—

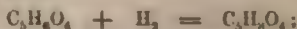


Pyrotartaric or Methyl-succinic Acid, $\text{CH}_3.\text{CH}\left\langle \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CH}_2.\text{CO}_2\text{H} \end{smallmatrix} \right.$

is obtained by the dry distillation of tartaric acid, mixed with an equal weight of powdered pumice; synthetically, also, from propene bromide, through the medium of the cyanide:—

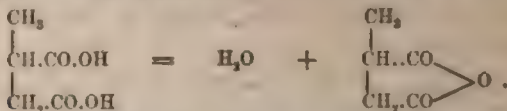


also by the action of nascent hydrogen on the three isomeric acids, itaconic, citraconic, and mesaconic:—



and lastly, by treating allyl iodide with potassium cyanide, and boiling the resulting nitril with a caustic alkali.

It crystallizes in small rhombic prisms, easily soluble in water, alcohol, and ether, melts at 112°C . (233.6°F .), and when rapidly heated is resolved into water and pyrotartaric anhydride, which distils over, and boils at 230°C . (446°F .).



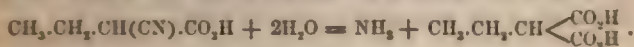
On heating it for a longer time to 2000 – 2100°C . (3920 – 4100°F .), or on exposing its aqueous solution, mixed with a uranium-salt, to sunshine, it is restored into CO_2 and butyric acid, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{H}$.

Neutral calcium pyrotartrate, $\text{C}_5\text{H}_6\text{O}_4.\text{Ca} + 2\text{H}_2\text{O}$, and the acid potassium salt, $\text{C}_5\text{H}_5\text{O}_4.\text{K}$, are sparingly soluble in water.

Normal Pyrotartaric Acid, $\text{CH}_2\left\langle \begin{smallmatrix} \text{CH}_2.\text{CO}.\text{OH} \\ \text{CH}_2.\text{CO}.\text{OH} \end{smallmatrix} \right.$ also called glutaric acid, is formed by heating propene cyanide, $\text{CH}_2\left\langle \begin{smallmatrix} \text{CH}_2.\text{CN} \\ \text{CH}_2.\text{CN} \end{smallmatrix} \right.$ with strong hydrochloric acid, to 100° , in a sealed tube for three or four hours. The contents of the tube are then evaporated down on a water-bath, treated with absolute alcohol to separate ammonium chloride, and the alcoholic solution is evaporated down, whereupon the acid is left as a thick brown syrup, which very slowly crystallizes. It may be purified by conversion into silver salt, and separation therefrom by hydrogen sulphide. The same acid is obtained by heating oxyglutaric acid (*q. v.*), with concen-

ated hydriodic acid to 120° C. (248° F.). It forms large transparent monoclinic crystals, easily soluble in water, melting at 97° C. (206.6° F.), and decomposing above 280° C. (536° F.) into water and the anhydride, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2\text{CO} \\ \text{CH}_2\text{CO} \end{smallmatrix} \text{O}$.

Ethylmalonic Acid, $\text{CH}_3\text{CH}_2\text{CH} \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$, is prepared from α -bromobutyric acid (p. 703), through the medium of the cyano-compound:



It crystallizes in colorless prisms, resembling pyrotartaric acid, and melting, like the latter, at 112° C. (233.6° F.). When heated to 160°, it is resolved into CO_2 and butyric acid. The calcium salt, $\text{C}_5\text{H}_8\text{O}_4\text{Ca} + \text{H}_2\text{O}$, forms prisms more soluble in cold than in hot water. The barium salt is anhydrous. The copper salt, $\text{C}_5\text{H}_8\text{O}_4\text{Cu} + \text{H}_2\text{O}$, crystallizes in beautiful tablets.

Dimethyl-malonic Acid, $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{H})_2$, prepared from bromisobutyric acid, is less soluble in water than either of the two preceding acids. It decomposes when melted, but does not yield butyric acid.

Substitution-products of the Pyrotartaric Acids.—Isomeric chloro- and bromo-derivatives of these acids are formed by direct addition of HCl , HBr , and Br_2 , to the unsaturated acids, $\text{C}_5\text{H}_6\text{O}_4$, viz., itaconic, citraconic, and mesaconic acids, these products being called respectively *ita*-, *citra*-, and *mesa*-derivatives of the pyrotartaric acids.

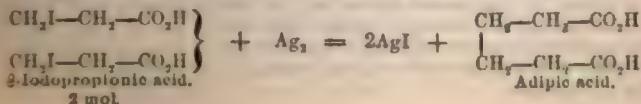
The monochlorinated derivatives, $\text{C}_5\text{H}_7\text{ClO}_4$, are formed by treating the three isomeric acids, $\text{C}_5\text{H}_6\text{O}_4$, with strong hydrochloric acid. They are all crystalline.—*Itachloropyrotartaric acid* melts at 145° C. (293° F.), and when heated with water or alkalis, is converted into itamalic acid, $\text{H}_2(\text{OH})\text{O}_4$.—*Citrachloropyrotartaric acid* is very unstable, and when heated with water gives up HCl , and passes into mesaconic acid, $\text{C}_5\text{H}_6\text{O}_4$ (p. 755). By boiling with alkalis, it is resolved into CO_2 , HCl , and methacrylic acid, $\text{C}_4\text{H}_6\text{O}_2$.—*Mesachloropyrotartaric acid* is more stable than the last, melts at 129° C. (264.2° F.), and is converted by heating with water into mesamalic acid, $\text{C}_5\text{H}_8\text{O}_5$.

The three isomeric dibromopyrotartaric acids differ from one another in their degree of solubility in water. The ita-compound is converted, by boiling the aqueous solution of its sodium salt, into aconic acid, $\text{C}_5\text{H}_4\text{O}_4$. The citra- and mesa-compounds, on the other hand, yield bromocrotonic acid, $\text{C}_4\text{H}_5\text{BrO}_3$.

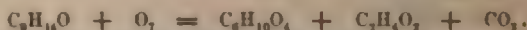
All these chloro-derivatives, and the corresponding bromo- and iodo-pyrotartaric acids, are converted by nascent hydrogen into ordinary pyrotartaric acid.

The constitution of the substituted pyrotartaric acids will be understood from that of the three isomeric acids, $\text{C}_5\text{H}_6\text{O}_4$ (p. 754).

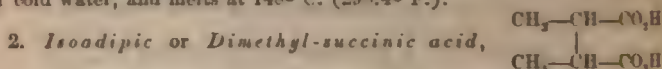
Adipic Acids, $\text{C}_6\text{H}_{10}\text{O}_4 = \text{C}_6\text{H}_8 \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$.—1. *Normal Adipic acid*, $\text{CO}_2\text{H}-(\text{CH}_2)_4-\text{CO}_2\text{H}$, originally obtained by the oxidation of fats with nitric acid, is formed synthetically by heating β -iodo-propionic acid with finely divided silver:



It is also produced by the action of nascent hydrogen on hydro-muconic acid, $C_6H_4O_4$; by oxidizing sebacic acid with nitric acid; and, together with acetic acid and carbon dioxide, by oxidation of phorone with chromic acid:



This acid crystallizes in shining laminae or prisms, dissolves in 13 parts of cold water, and melts at $148^\circ C.$ ($298.4^\circ F.$).



produced by heating α -bromopropionic acid, $CH_3-CHBr-CO_2H$, with finely divided silver, forms a thick syrup which does not readily crystallize.

The higher acids of this series are formed by the oxidation of stearic acid, oleic acid, and other acids of the fatty and acrylic series with nitric acid,—succinic acid and some of the lower homologues being generally formed at the same time. The mixed acids thus obtained are separated by fractional crystallization from ether, the higher members separating out first.

Pimelic Acid, $C_7H_{12}O_4$, is also produced by fusing camphoric acid with potash. It melts at $114^\circ C.$ ($237.2^\circ F.$), and dissolves in 40 parts of cold water.

Suberic Acid, $C_8H_{14}O_4$, is most readily obtained by boiling cork with nitric acid. It crystallizes in long needles or plates, melts at $140^\circ C.$ ($284^\circ F.$), and sublimes without decomposition between 1500 – $1600^\circ C.$ (3020 – $3200^\circ F.$). It dissolves in 100 parts of cold water, easily in hot water, alcohol, and ether.

An isomeric acid, tetramethylsuccinic acid,
$$\begin{array}{c} (CH_3)_2C-CO_2H \\ | \\ (CH_3)_2C-CO_2H \end{array}$$
 is formed by heating bromisobutyric acid $(CH_3)_2CBr.CO_2H$, with reduced silver. It melts at $95^\circ C.$ ($203^\circ F.$), and dissolves in 45 parts of water at $100^\circ C.$ ($500^\circ F.$).

A third isomeride, diethylsuccinic acid,
$$\begin{array}{c} C_2H_5.CH.CO_2H \\ | \\ C_2H_5.CH.CO_2H \end{array}$$
 is formed in like manner from α -bromobutyric acid, $C_2H_5.CHBr.CO_2H$.

Anchoic Acid, or **Lepargylic Acid**, $C_9H_{16}O_4$, is formed, together with other products, by the action of nitric acid on Chinese wax and on the fatty acids of cocoa-nut oil.—**Azelaic acid**, obtained by oxidizing castor oil with nitric acid, has the same composition as anchoic acid, but differs so much from it in physical properties, that it must be regarded as an isomeric or allotropic modification.

Sebic or Sebacic Acid, $C_{10}H_{18}O_4$, is a constant product of the destructive distillation of oleic acid, olein, and all fatty substances containing those bodies; it is extracted by boiling the distilled matter with water, and is also formed by the action of potash on castor-oil (see p. 592). It forms small pearly crystals resembling those of benzoic acid. It has a faintly acid taste, is but little soluble in cold water, melts when heated, and sublimes unchanged.

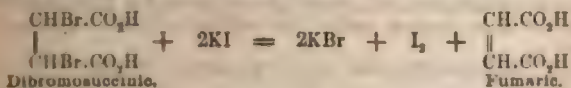
Brassylic Acid, $C_{11}H_{20}O_4$, obtained by oxidation of behenolic acid and succinic acid, melts at 1.08° , and is nearly insoluble in water.

Roccellic Acid, $C_{17}H_{32}O_4$, exists in *Roccella tinctoria*, and other lichens of the same genus, also in *Lecanora tartarea*, and is obtained by exhausting the first-mentioned plant with aqueous ammonia, precipitating the filtered liquor with calcium chloride, and decomposing the resulting calcium salt with hydrochloric acid. When purified by solution in ether, it forms white, rectangular, four-sided tabular crystals, melting at 132° C. (269.6° F.), and subliming at 200° C. (392° F.), being partially converted at the same time into an oxide, $C_{17}H_{30}O_3$. This acid decomposes carbonates.

2. Unsaturated Acids, $C_nH_{2n-4}O_4$, or $C_nH_{2n-2} \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$.—This series includes the following groups of isomeric acids:

| | |
|--|-------------|
| Fumaric and Maleic acids | $C_4H_4O_4$ |
| Itaconic, Citraconic, Mesaconic, and Paraconic acids | $C_5H_6O_4$ |
| Hydromuconic acid | $C_6H_8O_4$ |

These acids are capable of taking up two atoms of hydrogen, bromine, and other monad elements, and passing into the saturated acids of the succeeding series. A general method of forming them consists in heating the dibrominated derivatives of the acids, $C_nH_{2n-2}O_4$, with solution of potassium iodide; e. g.:



The isomeric modifications of these acids are determined by the structure of the radicles C_nH_{2n-2} , associated with the two carboxyl groups.

Fumaric and Maleic Acids, $C_4H_4O_4$.

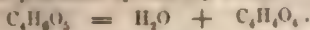


Fumaric.



Maleic.

These two acids are produced by the dry distillation of malic acid:



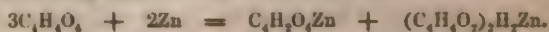
When malic acid is heated in a small retort nearly filled with it, it melts, boils, and gives off water, together with maleic acid and maleic anhydride, which pass over into the receiver, and dissolve in the water. After a time, small solid, crystalline scales make their appearance in the boiling liquid, and increase in quantity until the whole becomes solid. The process may now be interrupted, and the contents of the retort, after cooling, treated with cold water: unaltered malic acid is thereby dissolved out, and fumaric acid, which is less soluble, remains behind.

Fumaric acid exists, in the free state, in several plants, as in the common fumitory (*Fumaria officinalis*), Iceland moss (*Cetraria islandica*), and in certain fungi. It is produced also, as above stated, by the action of potassium iodide on dibromosuccinic acid, and from monobromosuccinic and alphasuccinic acids by fusion with potash.

Fumaric acid forms small, white, crystalline laminæ, which dissolve freely in hot water and alcohol, but require for solution about 200 parts of cold water: it is unchanged by hot nitric acid. When heated in a current of air, it sublimes, but by distillation in a retort, it is resolved in water and maleic anhydride, $C_4H_2O_3$. Similar differences are often observed in the behavior of organic bodies of small volatility, according as they are heated in close vessels or in a current of air. Fumaric acid is converted by sodium amalgam, hydriodic acid, and other hydrogenizing agents, into ordinary succinic acid. It unites, in presence of water, with metallic zinc, forming succinate of zinc, $C_4H_4O_4Zn$.

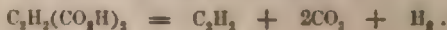
Fumaric acid forms acid and neutral metallic salts. The calcium and barium salts are anhydrous. The silver salt, $C_4H_2O_4Ag_2$, is quite insoluble in water. The ethylic ether, $C_4H_4O_4(C_2H_5)_2$ is a liquid boiling at $225^\circ C.$ ($437^\circ F.$).

Maleic Acid, $H_2C=C<\begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}$, crystallizes in large prisms or tables, very soluble in water, alcohol, and ether, and having a strong acid taste and reaction. It is converted by heat into fumaric acid, by nascent hydrogen into succinic acid, and by bromine into dibromosuccinic acid, $H_2BrC-CHBr(CO_2H)_2$. Its aqueous solution dissolves zinc without evolution of hydrogen, forming maleate and succinate of zinc:

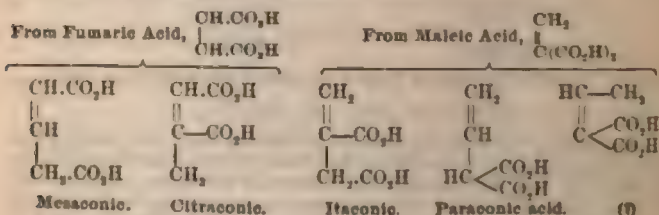


Maleic anhydride, $C_4H_2O_3$, crystallizes in large laminæ or needles, melts at $57^\circ C.$ ($134.6^\circ F.$), boils without decomposition at $196^\circ C.$ ($384.8^\circ F.$) and is converted by water into maleic acid.

Maleic and fumaric acids are resolved by electrolysis of the concentrated solutions of their sodium salts into carbon dioxide, hydrogen and acetylene:—

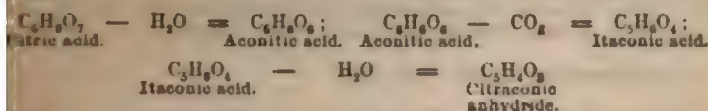


Acids. $C_3H_2O_4 = C_3H_2<\begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}$.—Theory indicates the existence of five isomeric acids of this form, and of these four are known, viz., citraconic and mesaconic acids, which may be derived from fumaric acid by interpolation of CH_2 , and itaconic and paraconic acids, derivable in like manner from maleic acid:—



Citraconic and itaconic acids are produced by the action of heat on citraconic acid. When crystallized citric acid is heated in a retort, it first melts in its water of crystallization, and then boils, giving off water. Afterwards, at about $175^\circ C.$ ($347^\circ F.$), vapors of acetone distil over, and a copious disengagement of carbon monoxide takes place. At this time the residue in the retort consists of aconitic acid. If the distillation be still continued, carbon dioxide is given off, and itaconic acid crystallizes in the neck of the retort. If these crystals be repeatedly distilled, an

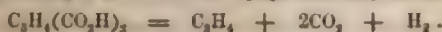
By mass of citraconic oxide or anhydride is obtained, which no longer solidifies. These decompositions are represented by the following equations:—



The citraconic anhydride when exposed to the air absorbs moisture, and is converted into crystallized citraconic acid, $\text{C}_5\text{H}_6\text{O}_4$.

Mesaconic acid is produced by boiling itaconic acid with weak nitric acid. These three isomeric acids are all converted by nascent hydrogen into pyrotartaric acid, $\text{C}_4\text{H}_4\text{O}_6$. They also take up a molecule of HBr , HCl , HI , forming isomeric monobromopyrotartaric acids, H_2BrO_4 , etc., or of bromine, Br_2 , forming isomeric dibromopyrotartaric acids. Itaconic and citraconic acids are, however, more inclined to these transformations than mesaconic acid, which is altogether a more stable compound.

On subjecting their potassium salts to electrolysis, the three acids are decomposed, yielding a hydrocarbon, C_2H_4 , according to the equation:—



Now, citraconic acid thus treated yields ordinary allylene, $\text{CH}=\text{C}-\text{CH}_3$, whereas itaconic acid yields iso-allylene or allene, $\text{CH}_2=\text{C}=\text{CH}_2$, both of which are in accordance with the formulæ above given for these acids. Mesaconic acid likewise yields allylene, as might be expected, since the hydrocarbon, $\text{CH}=\text{CH}-\text{CH}_3$, cannot exist.

Itaconic Acid is most easily prepared by heating citraconic anhydride with water to 130° – 140°C . (266° – 284°F). It crystallizes in rhombic prisms, dissolves in 17 parts of water at 10°C . (50°F), melts at 61°C . (321.8°F), and is resolved by distillation into water and citraconic anhydride.

Citraconic Acid crystallizes in four-sided prisms, melting at 80°C . (176°F). It is much more soluble in water than itaconic acid, and deliquesces on exposure to the air. Its anhydride, $\text{C}_5\text{H}_4\text{O}_3$, forms an oily liquid, which easily recombines with water to form the acid.

Mesaconic Acid forms shining prisms sparingly soluble in water, melts at 208°C . (406.4°F), and sublimes without decomposition. It is not readily obtained by the action of heat on citrachloropyrotartaric acid.

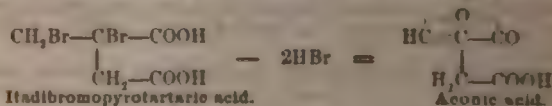
Paraconic Acid is formed, together with itamalic acid, $\text{C}_5\text{H}_6\text{O}_5$, by heating itachloropyrotartaric acid, $\text{CH}_2\text{Cl}-\text{CH}(\text{CO}_2\text{H})-\text{CH}_2\text{CO}_2\text{H}$, with water. It is easily soluble in water, melts at 70°C . (158°F), and is resolved by distillation into water and citraconic anhydride. It unites with HBr , forming itabromopyrotartaric acid. When heated with alkalis it takes up water, and forms itamalic acid, $\text{C}_5\text{H}_6\text{O}_5$.

The constitution of paraconic acid is probably represented either by the fourth or the fifth formula above given; but there is at present no means of deciding between the two. Moreover, it is not easy to see how an acid having its two carboxyl groups associated with the same carbon-atom could be formed from itabromopyrotartaric acid, unless the reaction were accompanied by molecular transposition.

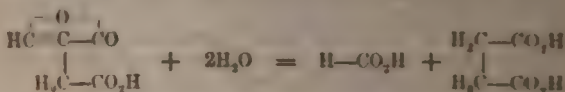
Hydromuconic Acid, $C_6H_8O_6 = C_6H_6(CO_2H)_2$, produced by the action of sodium-amalgam on dichloromuconic acid, $C_6H_4Cl_2O_4$, crystallizes in large prisms, slightly soluble in cold water, and melting at $135^\circ C.$ ($275^\circ F.$). It is converted by sodium-amalgam into adipic acid, $C_6H_{10}O_6$, and unites with bromine, forming dibromadipic acid, $C_6H_4Br_2O_4$.

3. Unsaturated Acids, $C_nH_{2n-6}O_4$.

Aconic Acid, $C_5H_4O_4$.—This acid is formed by boiling itadibromopropars tartaric acid with caustic soda. It is very soluble in water, alcohol, and ether, and crystallizes from the alcoholic solution in foliate groups of thin needles, melting at $154^\circ C.$ ($309.2^\circ F.$). From its origin it might be expected to be a bibasic acid; but it is really monobasic, its silver salt being $C_5H_3O_4Ag$, and its barium salt $(C_5H_3O_4)_2Ba$. This may perhaps be explained by regarding the acid as an anhydro-acid similar to dilactic acid, its mode of formation being represented by the following equation:



By boiling with baryta-water, aconic acid is resolved into formic and succinic acids:



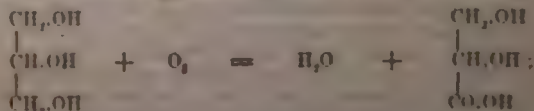
Muconic Acid, $C_6H_8O_6$, formed in like manner from dibromadipic acid, forms large crystals melting at $100^\circ C.$ It is monobasic, like aconic acid, and is probably constituted in a similar manner. By boiling with baryta-water it is resolved into acetic and succinic acids.

Triatomic Acids.

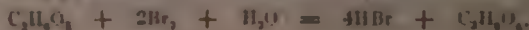
1. Monobasic, $C_nH_{2n+1}O_3$.

These acids are derived from the triatomic alcohols $C_nH_{2n+1}O_3$ (glycerins) by substitution of O for H_2 , in the same manner as the acids of the diatomic series, $C_nH_{2n}O_4$, from the glycols, $C_nH_{2n+2}O_2$. There is, however, but one acid of the series at present known, viz.:

Glyceric Acid, $C_3H_5O_4$ (dioxypropionic acid), which is formed by the gradual oxidation of glycerin with nitric acid:



also by heating glycerin to $100^\circ C.$ in a sealed tube, with bromine and water:



are it, nitric acid (specific gravity 1.5), is poured through a long-funnel to the bottom of a tall glass jar containing glycerin, diluted (equal bulk of water (100 grains of glycerin, 100 of water, and 100 of red nitric acid, are good proportions). The two layers of liquid mix, and assume a blue color, and the oxidation of the glycerin is accompanied by copious evolution of gas; if the liquid becomes too violent, the action must be moderated by external cooling. When the action is completed, which takes five or six days, the acid liquid is evaporated to a syrup, diluted with water, saturated at the boiling heat with a small quantity of milk of lime, and then filtered. The condensed filtrate deposits calcium glycerate in warty crusts, from which pyruvic acid may be separated by boiling with oxalic acid. The liquid from the calcium oxalate is boiled with lead oxide to remove any excess of oxalic acid, then treated with hydrogen sulphide to precipitate dissolved lead, and the filtered liquid is evaporated over the water-

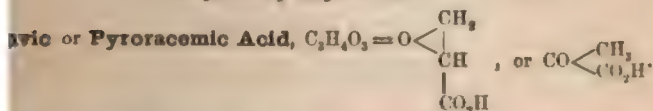
pyruvic acid when concentrated is a colorless, uncrystallizable syrup, soluble in water and in alcohol. Heated above 140°C . (284°F .), it decomposes, yielding water, pyruvic acid, and pyrotartaric acid. By boiling with potash it is resolved into acetic and formic acids; by boiling with aqueous potash, it yields oxalic and lactic acids, and by the action of phosphorus iodide it is converted into 2-iodopropionic acid.

Metallic glycerates are soluble in water, and crystallize well. They are reddened by ferrous salts, and are thereby distinguished from the tartarates, from which they differ only by the elements of water. The calcium salt, $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Ca} + 2\text{H}_2\text{O}$, usually crystallizes in nodular groups of crystals, easily soluble in water: the lead salt, $(\text{C}_3\text{H}_5\text{O}_4)_2\text{Pb}$, is but slightly soluble in water.

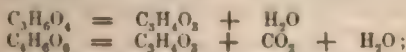
Ethyl pyruvate, $\text{C}_3\text{H}_5\text{O}_4 \cdot \text{C}_2\text{H}_5$, obtained by heating glycerin with absolute alcohol, is a thick liquid, having a specific gravity of 1.193 at 0° , and boiling at $230^{\circ}\text{--}240^{\circ}\text{C}$. ($446^{\circ}\text{--}464^{\circ}\text{F}$.).

Glycylglycine, $\text{CH}_2\text{NH}_2\text{—CH.OH—CO.OH}$, or serine, is obtained by boiling sericin or silk-gelatin (*q. v.*), with dilute sulphuric acid. It forms hard crystals, soluble in water, but insoluble in alcohol. It unites both with acids and with bases. Nitrous acid converts it into glycolic acid.

Anhydrides of Glyceric Acid.



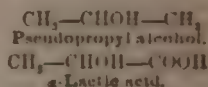
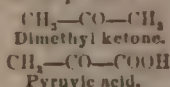
Pyruvic anhydro-acid is formed, together with other products, by the dry distillation of glyceric, tartaric, or racemic acid:



Pyruvic acid is obtained pure by redistilling the product several times, and collecting the portion which passes over between 165° and 170°C . ($329^{\circ}\text{--}336^{\circ}\text{F}$.). It is a yellowish liquid, easily soluble in water, alcohol, and ether, and smells like acetic acid, and boils with partial decomposition at 70° . It is monobasic, and forms salts which crystallize well, provided that heat is avoided in their preparation; but their solutions, if

evaporated by heat, leave gummy uncrystallizable salts, which yield a syrupy non-volatile modification of the acid, likewise obtained when an aqueous solution of the original acid is evaporated by heat. This syrupy acid, which is probably a polymeric modification, is resolved by heat into carbon dioxide and pyrotartaric acid, $2C_3H_4O_3 = CO_2 + C_3H_4O_4$.

Pyruvic acid is converted by nascent hydrogen into ordinary lactic acid, $CH_3-CH(OH)-COOH$, and may therefore be regarded as a ketonic acid related to lactic acid in the same manner as dimethyl-ketone (acetone) to secondary propyl alcohol, as represented by the second of the constitutional formulæ given on p. 757:

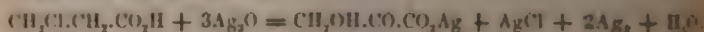


The reaction, however, agrees equally well with the first formula, which represents pyruvic acid as an anhydride of glyceric acid, from which it is formed by actual dehydration.

Pyruvic acid is converted by phosphorus pentachloride into dichloropropionic chloride, $CH_2Cl-CHCl-COCl$; by hydrochloric acid at 100° into carbon dioxide and pyrotartaric acid; by oxidizing agents into oxalic acid; by boiling with baryta-water into uvicic acid, $C_8H_8O_8 = C_8H_7 \left\{ \begin{array}{l} CH \\ (CO_2H) \end{array} \right\}_2$, an acid belonging to the aromatic group.

The pyruvates crystallize well, provided that heat is avoided in their preparation. The sodium salt, $C_3H_3O_3Na$, forms large anhydrous prisms. The lead salt, $(C_3H_3O_3)_2Pb$, is a crystalline precipitate. The silver salt is also crystalline.

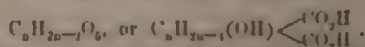
Oxypyruvic or Carbacetoxylic Acid, $C_4H_4O_4$ or $CH_2OH-CO-CO_2H$, isomeric with malonic acid, is formed by heating β -chloropropionic acid with excess of silver oxide:



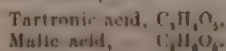
It forms a syrup, easily soluble in water and in ether. It is monobasic; its barium salt crystallizes in spherical nodules; the lead salt in crystals, the zinc salt in shining scales.

The acid is converted by nascent hydrogen into glyceric acid, and by hydriodic acid at 200° C. (392° F.) into pyruvic acid.

TRIATOMIC AND BIBASIC ACIDS.



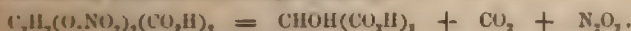
The acids of this series may be formed from those of the oxalic or succinic series, $C_nH_{2n}(CO_2H)_2$, by substitution of OH for H. Four of them are at present known, viz.:



Tartronic Acid, $CH(OH) \begin{array}{l} < CO_2H \\ < CO_2H \end{array}$ (oxymalonic acid), is formed by the action of nascent hydrogen on mesoxalic acid (p. 747):



also by spontaneous decomposition of dinitrotartaric acid, when its aqueous solution is left to evaporate, the decomposition being attended with evolution of carbon dioxide and nitrogen dioxide:



Tartronic acid crystallizes in large prisms, which melt at $175^\circ C.$ ($347^\circ F.$), and are resolved at higher temperatures into carbon dioxide, water, and glycolide:

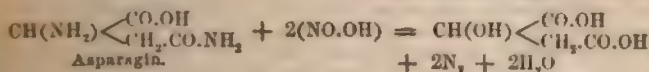
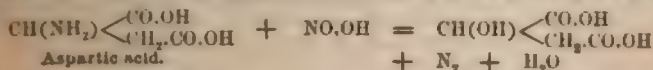


Malic Acid, $C_4H_6O_5 = C_2H_5(OH) \begin{smallmatrix} CO_2H \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CO_2H \\ \diagup \end{smallmatrix} = CH(OH) \begin{smallmatrix} CO_2H \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CO_2H \\ \diagup \end{smallmatrix} C_2H_5CO_2H$.

Ornithic acid.—This acid is formed synthetically by the action of moist silver oxide on bromosuccinic acid:



It is also produced by deoxidation of tartaric acid, $C_4H_6O_6$, with hydriodic acid, and by the action of nitrous acid on aspartic acid, $C_4H_7NO_4$ (amidosuccinic acid), or on asparagin, $C_4H_8N_2O_3$, which is the amide of the latter:



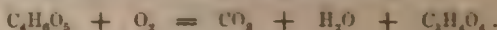
Malic acid is the acid of apples, pears, and various other fruits: it is often associated with citric acid. It may be advantageously prepared from the juice of the garden rhubarb, in which it exists in large quantity, accompanied by acid potassium oxalate. The rhubarb stalks are peeled, and ground or grated to pulp, which is subjected to pressure. The juice is heated to the boiling point, neutralized with potassium carbonate, and mixed with calcium acetate: insoluble calcium oxalate then falls, and may be removed by filtration. To the clear and nearly colorless liquid, solution of lead acetate is added as long as a precipitate continues to be produced, and the lead malate is collected on a filter, washed, diffused through water, and decomposed by sulphuretted hydrogen. The filtered liquid is carefully evaporated to the consistence of a syrup, and left in a dry atmosphere till it becomes converted into a solid and somewhat crystalline mass of malic acid. From the berries of the mountain ash (*Sorbus aucuparia*), in which malic acid is likewise present in considerable quantity, especially at the time they begin to ripen, the acid may be prepared by the same process.

Malic acid crystallizes in groups of colorless prisms, slightly deliquescent and very soluble in water; alcohol also dissolves it. The aqueous solution has an agreeable acid taste: it becomes mouldy and spoils by keeping.

Malic acid, as it exists in plants, and as obtained from active tartaric acid, from asparagin, or from aspartic acid produced from the latter, exerts a rotatory action on polarized light: $[\alpha] = -5^\circ$; but by the action of nitrous acid on inactive aspartic acid (resulting from the decomposition of fumarinide), Pasteur has obtained a modification of malic acid which is optically inactive. Malic acid formed from succinic acid is also inactive.

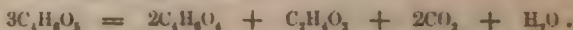
Malic acid when heated gives off water at $130^\circ C.$ ($266^\circ F.$), and at $175^\circ C.$ ($347^\circ F.$) a distillate of maleic acid and maleic anhydride, while fumaric

acid remains behind (p. 754). By slow oxidation with a cold solution of potassium chromate, it is converted into maleic acid:—



Nitric acid readily converts it into oxalic acid, with evolution of carbon dioxide.

By the action of reducing agents, most readily by heating with strong hydriodic acid, malic acid is reduced to succinic acid; also by fermentation of its calcium salt in contact with putrefying cheese, acetic acid and carbon dioxide being also produced:—



The sodium salt of bromomalic acid, $C_4H_3BrO_3$, obtained by boiling an aqueous solution of sodium dibromosuccinate, $(C_4H_3NaBr_2O_4)$, is converted by boiling with lime-water into the calcium salt of tartaric acid, $C_4H_2O_6$.



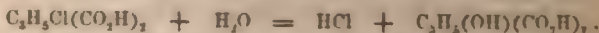
Malic acid forms both acid and neutral salts. Those formed from the optically active acid are likewise active, some being dextro-, others levo-rotatory. The most characteristic of the malates are *acid ammonium malate*, $C_4H_3(NH_4)O_3$, which crystallizes remarkably well, and *lead malate*, $C_4H_2PbO_6 \cdot 3Aq.$, which is insoluble in pure water, but dissolves to a considerable extent in warm dilute acids, and separates on cooling in brilliant silvery crystals containing water. By this character the acid may be distinguished. *Acid calcium malate*, $C_4H_2O_6Ca \cdot C_4H_2O_6 + 8H_2O$, is also a very beautiful salt, freely soluble in warm water. It is prepared by dissolving the sparingly soluble *neutral malate* in hot dilute nitric acid, and leaving the solution to cool.

Diethyl malate, $C_4H_4(C_2H_5)_2O_3$, is a liquid which is partially decomposed by distillation, and is converted by acetyl chloride into diethyl acetomalate, $C_2H_5(OC_2H_5)O < \begin{smallmatrix} CO_2C_2H_5 \\ CO_2C_2H_5 \end{smallmatrix}$.

Oxyprotartrario Acid, $C_5H_6O_3 = C_3H_5(OH) < \begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}$, is produced by boiling dicyanhydrin, $C_3H_5(OH)(CN)_2$, (p. 612) with alkalis. It forms crystals, easily soluble in water, alcohol, and ether, and melting at $135^\circ C.$ ($275^\circ F.$).

Isomeric with it are four bibasic acids of unknown structure, called *isomalic*, *citrarmalic*, *mesamalic*, and *oxyglutaric* acids.

Ita- and *mesamalic* acids are formed by boiling the corresponding chloropyrotartaric acids (p. 751) with water or solution of sodium carbonate:—



Both form deliquescent crystals, melting at $60^\circ C.$ ($140^\circ F.$).

Citrarmalic acid is produced by the action of zinc on chlorocitrarmalic acid, $C_3H_2ClO_3$ (formed by addition of hypochlorous acid, $ClOH$, to citraconic acid, $C_3H_4O_4$). It is a deliquescent mass.

Oxyglutaric acid, $C_5H_7(OH)O_4$, produced by the action of nitrous acid on amidoglutaric acid, $C_5H_7(NH_2)O_4$, crystallizes with difficulty, and is converted by hydriodic acid into glutaric acid (p. 750).

Amidoglutaric acid, or *Glutamic acid*, $C_5H_7(NH_2)O_4 = C_3H_5(NH_2) < \begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}$, occurs, together with aspartic acid, in the molasses of sugar-beet, and is formed by boiling albuminous bodies with dilute sulphuric acid. It forms shining rhombic octohedrons, moderately soluble in water, insoluble in

alcohol and ether, melting with partial decomposition at 140°C . (284°F). It unites both with bases and with acids, and is converted by nitrous acid into oxyglutaric acid.

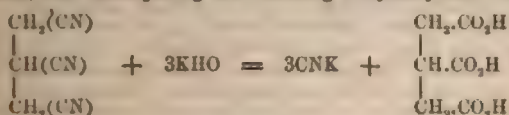
Oxyadipic Acid, $\text{C}_6\text{H}_{10}\text{O}_5 = \text{C}_4\text{H}_7(\text{OH})\begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$, is a deliquescent mass formed by the action of moist silver oxide on monobromadipic acid.

Oxymaleic Acid, $\text{C}_4\text{H}_4\text{O}_5 = \text{C}_2\text{H}(\text{OH})\begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{smallmatrix}$, is an unsaturated triatomic and bibasic acid, produced by the action of silver oxide on bromomaleic acid (p. 754). It crystallizes in slender needles, easily soluble in water, alcohol, and ether. An acid isomeric with it is formed from bromoisomaleic acid.

TRIATOMIC AND TRIBASIC ACIDS.

Only one saturated acid of this group is known, viz.:

Tricarballic Acid, $\text{C}_6\text{H}_6\text{O}_6 = \text{C}_3\text{H}_3(\text{CO}_2\text{H})_3$, which is produced: 1. By heating allyl tribromide, $\text{CH}_2\text{Br}-\text{CHBr}-\text{CH}_2\text{Br}$, with potassium cyanide, and decomposing the resulting tricyanhydrin with potash:



2. By the action of sodium-amalgam on aconitic acid, $\text{C}_6\text{H}_6\text{O}_6$. 3. By reduction of citric acid, $\text{C}_6\text{H}_8\text{O}_7$, with hydriodic acid.

Tricarballic acid crystallizes in colorless rhombic prisms, easily soluble in water and alcohol, slightly soluble in ether. The tricarballicates of the alkali-metals are easily soluble in water, the rest insoluble or sparingly soluble. The *ethylic ether*, $\text{C}_3\text{H}_5(\text{CO}_2\text{C}_2\text{H}_5)_3$, is a liquid boiling between 295°C and 305°C . (563° – 581°F).

The following tribasic acids are unsaturated compounds:

Aconitic Acid, $\text{C}_6\text{H}_6\text{O}_6 = \text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$, exists in monk's-hood (*Aconitum Napellus*), and other plants of the same genus, also in *Equisetum flavatile*, and is one of the products obtained by the dehydration of citric acid (p. 353): $\text{C}_6\text{H}_8\text{O}_7 - \text{H}_2\text{O} = \text{C}_6\text{H}_6\text{O}_6$.

When crystallized citric acid is heated in a retort till it begins to become colored, and to undergo decomposition, and the fused, glassy product, after cooling, is dissolved in water, aconitic acid remains as a white, confusedly crystalline mass, which may be purified by converting it into a lead salt, and decomposing the latter with hydrogen sulphide.

Aconitic acid crystallizes in small laminae, very soluble in water, alcohol, and ether. It melts at 140°C . (284°F), and decomposes at a higher temperature into carbon dioxide, itaconic acid, and citraconic anhydride. Nascent hydrogen converts it into tricarballic acid.

Aconitic acid forms three series of salts. The *tertiary lead-salt*, $(\text{C}_6\text{H}_4\text{O}_6)_2\text{Pb}$, is insoluble in water. The *calcium salt*, $(\text{C}_6\text{H}_4\text{O}_6)_2\text{Ca}_3 + 6\text{H}_2\text{O}$, which is sparingly soluble, occurs abundantly in the expressed juice of monk's-hood: the magnesium salt in that of *Equisetum*. The *ethylic ether*, $\text{C}_6\text{H}_4\text{O}_6(\text{C}_2\text{H}_5)_3$, is a liquid boiling at about 236°C . (456.80°F).

The isomeric acid, **aconitic acid**, formed by the action of sodium on ethylic monobromacetate, crystallizes in slender needles, and forms salts differing in some respects from the aconitates.

Chelidonic Acid, $C_7H_6O_6 = C_6H(CO_2H)_2$, occurs as a calcium salt, together with malic and fumaric acids, in *Chelidonium majus*, and is extracted by boiling the juice, filtering, adding nitric acid, precipitating with lead nitrate, and decomposing the resulting lead salt with hydrogen sulphide. It crystallizes in silky needles containing 1 molecule of H_2O , sparingly soluble in cold water and alcohol. It is decomposed by bromine water, yielding oxalic acid, bromoform, and pentabromacetone, C_5HBr_5O .

Meconic Acid, $C_7H_6O_7 = C_6H(CO_2H)_2$ (oxychelidonic acid), is a tribasic acid existing in opium. To prepare it, the liquid obtained by exhausting opium with water, is neutralized with powdered marble and precipitated by calcium chloride; and the calcium meconate thus precipitated is suspended in warm water and treated with hydrochloric acid; on cooling, impure meconic acid crystallizes, and may be purified by repeated treatment with hydrochloric acid. The pure acid crystallizes in mica-like plates, easily soluble in boiling, difficultly soluble in cold water, soluble likewise in alcohol. The crystals contain $C_7H_6O_7 + 3H_2O$, and give off their water at 100° ; the dehydrated acid melts at 150° C. (302° F.).

Meconic acid forms three series of salts. There are two *silver meconates*, one yellow, containing $C_7HAg_2O_7$; the other white, consisting of $C_7H_2Ag_2O_7$. Meconic acid produces a deep red color with ferric salts. By the action of sodium-amalgam it is converted into hydromeconic acid, $C_7H_{10}O_7$.

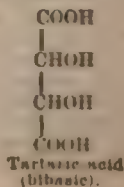
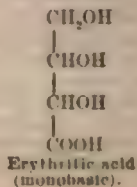
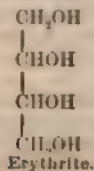
Comenic Acid, $C_6H_4O_3$, is a product of decomposition of meconic acid. When an aqueous, or, better, a hydrochloric solution of meconic acid is boiled, carbon dioxide is evolved, and the solution now contains comenic acid, which crystallizes on cooling, being very difficultly soluble in cold water. The same acid may be obtained by heating meconic acid to 200° C. (392° F.). It is bibasic; its formation is represented by the equation $C_7H_6O_7 = C_6H_4O_3 + CO_2$.

Pyromeconic or Pyrocomenic Acid, $C_6H_4O_3$, is a monobasic acid, formed by submitting either comenic or meconic acid to dry distillation, one molecule of carbon dioxide being evolved in the former case and two in the latter.

Pyrocomenic acid is a weak acid; it is soluble in water and alcohol. from these solutions it crystallizes in long colorless needles, which melt at 120° C. (248° F.), and begin to sublime at the boiling point of water. Both comenic and pyrocomenic acids exhibit the red coloration with ferric salt.

Tetratomic Acids.

These acids may be derived from tetratomic alcohols by substitution of one, two, three, or four atoms of oxygen for a corresponding number of hydrogen molecules:



Only one tetratomic acid has, however, been actually formed by oxidation of the corresponding alcohol, namely, erythritic acid, $C_4H_5O_5$, from erythrite, $C_4H_{10}O_4$.

The known tetratomic acids belonging to the fatty group are—

| | |
|------------------------------|------------|
| Erythritic acid, $C_4H_5O_5$ | monobasic. |
| Dioxymalonic, $C_4H_4O_6$ | bibasic. |
| Tartaric, $C_4H_4O_6$ | |
| Homotartaric, $C_4H_4O_6$ | |
| Citric, $C_6H_8O_7$ | tribasic. |

Erythritic Acid, $C_4H_5O_5 = C_2H_4(OH)_2.CO_2H$, formed by the oxidation of erythrite, $C_4H_{10}O_4$ (p. 616), in aqueous solution in contact with platinum black, is a deliquescent crystalline mass, and is capable of forming salts containing 2 equivalents of metal.

Dioxymalonic Acid, $C_4H_4O_6 = C(OH)_2 \begin{smallmatrix} CO_2H \\ CO_2H \end{smallmatrix}$, formed by the action of moist silver oxide or dibromomalonic acid, is probably identical with the hydrate of mesoxalic acid (p. 747).

Tartaric Acid, $C_4H_4O_6 = \begin{smallmatrix} CHOH-CO_2H \\ | \\ CHOH-CO_2H \end{smallmatrix} = C_2H_2 \left\{ \begin{smallmatrix} (OH)_2 \\ (CO_2H)_2 \end{smallmatrix} \right.$ —This

formula includes four bibasic acids, distinguished from one another by certain physical properties, especially by their crystalline forms, and their action on polarized light—namely, Dextrotartaric acid, which turns the plane of polarization to the right; Levotartaric acid, which turns to the left with equal force; Paratartaric or Racemic acid, which is optically inactive, and separable into equal quantities of dextro- and levotartaric acids; and an inactive variety of tartaric acid, which is not thus separable.

1. **DEXTROTARTARIC OR ORDINARY TARTARIC ACID**.—This is the acid of grapes, tamarinds, pine-apples, and several other fruits, in which it occurs to the state of an acid potassium-salt: calcium tartrate is also occasionally met with. The tartaric acid of commerce is wholly prepared from *tartar emel*, an impure acid potassium tartrate, deposited from wine, or rather from grape-juice in the act of fermentation. This substance is purified by solution in hot water, with the aid of a little pipe-clay and animal charcoal, to remove the coloring matter of the wine, and subsequent crystallization: it then constitutes *cream of tartar*, and serves for the preparation of the acid. The salt is dissolved in boiling water, and powdered chalk is added as long as effervescence is excited, or the liquid exhibits an acid reaction; calcium tartrate and neutral potassium tartrate are thereby produced, and the latter is separated from the former, which is insoluble, by filtration. The solution of potassium tartrate is then mixed with excess of calcium chloride, which throws down all the remaining acid in the form of calcium salt: this is washed and added to the former portion, and the whole is digested with a sufficient quantity of dilute sulphuric acid to withdraw the base, and liberate the tartaric acid. The filtered solution is cautiously evaporated to a syrupy consistence, and left to crystallize in a warm place. Liebig found that tartaric acid is artificially produced by the action of nitric acid upon milk sugar.

Tartaric acid forms colorless, transparent monoclinic prisms often of large size; they are permanent in the air, and inodorous; they dissolve with great facility in water, both hot and cold, and are soluble also in alcohol. The solution reddens litmus strongly, and has a pure acid taste. The aqueous solution, as above mentioned, exhibits right-handed polarization.

This solution is gradually spoiled by keeping. The crystallized acid melts at 130°C . (275°F .), is converted at 170°C . (338°F .) into optically inactive mesotartaric acid, and when heated for some time to 180°C . (356°F .) gives off water, and yields anhydrides (p. 766). Tartaric acid is consumed in large quantities by the calico-printer, being employed to extract chlorine from solution of bleaching powder, in the production of white discharged patterns upon a colored ground.

Tartrates.—Tartaric acid, being tetratomic and bibasic, has only two hydrogen atoms replaceable by metals, the other two being replaceable by alcoholic or acid radicles. With monad metals it forms acid and neutral salts, $\text{C}_4\text{H}_4\text{M}'\text{O}_6$, and $\text{C}_4\text{H}_4\text{M}_2\text{O}_6$; with dyad metals, neutral salts, $\text{C}_4\text{H}_4\text{M}_2\text{O}_6$, and double salts, like *bario-potassic tartrate*, $\text{C}_4\text{H}_4\text{BaO}_6 \cdot \text{C}_4\text{H}_4\text{K}_2\text{O}_6$. With trisid metals it forms a peculiar class of salts, best known in the case of the *antimony-salt* (p. 764).

Potassium Tartrate.—The neutral salt, $\text{C}_4\text{H}_4\text{K}_2\text{O}_6$, may be obtained by neutralizing cream of tartar with chalk, as in the preparation of the acid, or by saturating cream of tartar with potassium carbonate. It is very soluble, and crystallizes with difficulty in right rhombic prisms, which are permanent in the air, and have a bitter, saline taste. The *acid and cream of tartar*, $\text{C}_4\text{H}_4\text{K}_2\text{O}_6$, the origin and preparation of which have been already described, forms irregular groups of small transparent or translucent prismatic crystals which grate between the teeth. It dissolves pretty freely in boiling water, but the greater part separates as the solution cools, leaving about $\frac{1}{5}$ or less dissolved in the cold liquid. The salt has an acid reaction and a sour taste. When exposed to heat in a closed vessel, it is decomposed, with evolution of inflammable gas, leaving a mixture of finely divided charcoal and pure potassium carbonate, from which the latter may be extracted by water. Cream of tartar is almost always produced when tartaric acid in excess is added to a moderately strong solution of a potassium-salt, and the whole agitated.

Sodium Tartrate.—Two of these salts are known—a neutral salt $\text{C}_4\text{H}_4\text{Na}_2\text{O}_6 + 2\text{Aq}$.; and an acid salt, $\text{C}_4\text{H}_3\text{NaO}_6 + \text{Aq}$. Both are easily soluble in water, and crystallizable. Tartaric acid and sodium bicarbonate form the ordinary effervescent draughts.

Potassium and Sodium tartrate: Rochelle or Saignette salt, $\text{C}_4\text{H}_4\text{KNaO}_6 + 4\text{Aq}$.—This beautiful salt is made by neutralizing a hot solution of cream of tartar with sodium carbonate, and evaporating to the consistence of the syrup. It separates in large transparent rhombic prisms with hemispherical faces; they effloresce slightly in the air, and dissolve in $1\frac{1}{2}$ parts of cold water. Acids precipitate cream of tartar from the solution. Rochelle salt has a mild saline taste, and is used as a purgative.

Ammonium Tartrate.—The neutral tartrate is a soluble and effervescent salt, containing $\text{C}_4\text{H}_4(\text{NH}_4)_2\text{O}_6 + \text{Aq}$. The acid tartrate, $\text{C}_4\text{H}_3(\text{NH}_4)\text{O}_6$, closely resembles ordinary cream of tartar. A salt analogous to Rochelle salt also exists, having ammonium in place of sodium.

The tartrates of calcium, barium, strontium, magnesium, and of most of the heavy metals, are insoluble, or nearly so, in water.

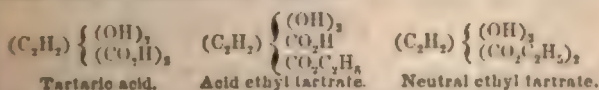
Potassio-antimonious Tartrate, or Tartar emetic, is easily made by boiling antimony trioxide in solution of cream of tartar: it is deposited from a hot and concentrated solution in rhombic octohedrons, which dissolve without decomposition in 15 parts of cold and 3 of boiling water.

have an acid, extremely disagreeable metallic taste. The solution is decomposed by both acids and alkalis: the former throws down a mixture of cream of tartar and antimony trioxide, and the latter the trioxide, which is again dissolved by great excess of the reagent. Sulphuretted hydrogen separates all the antimony in the state of trisulphide. The dry substance heated on charcoal before the blowpipe, yields a globule of metallic antimony. The crystals contain $2C_4H_4K(SbO)_3 + Aq.$, the group SbO acting as a univalent radicle, and replacing one atom of hydrogen. When dried at 100° , they give off their water of crystallization; and at 200° C. (392° F.) an additional molecule of water, leaving the compound, $C_4H_4K(SbO)_3$, which has the constitution of a salt, not of tartaric, but of tartaric acid, $C_4H_4O_6$. Nevertheless, when dissolved in water, the crystals again take up the elements of water, and reproduce the original salt. An analogous compound, containing arsenic in place of antimony, has also been obtained. It has the same crystalline form as tartar emetic.

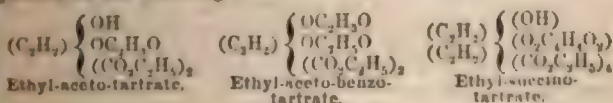
A solution of tartaric acid dissolves ferric hydrate in large quantity, forming a brown liquid, which has an acid reaction, and dries up by gentle heating to a brown, transparent, glassy substance, destitute of all traces of crystallization. It is very soluble in water, and the solution is not precipitated by alkalis, either fixed or volatile. Indeed, tartaric acid, added in sufficient quantity to a solution of ferric oxide, or alumina, entirely prevents the precipitation of the bases by excess of ammonia. Tartrate and potassium tartrate of iron are used in medicine, these compounds having a disagreeable taste than most of the iron preparations.

Solutions of tartaric acid give with lime and baryta-water, and with lead acetate, white precipitates, which dissolve in excess of the acid; with strontal calcium and barium salts no change is produced. Silver nitrate dissolves in neutral tartrates a white precipitate of silver tartrate, which dissolves in ammonia. On gently heating the solution, a bright metallic salt of silver is formed. The reaction of tartaric acid with solutions of potassium salts has been already noticed.

Tartaric Ethers.—1. Tartaric acid forms, with monatomic alcohols, acid and neutral ethers, in which one or both of the atoms of hydrogen in its molecule is replaced by an alcohol-radicle. These compounds may be formulated as follows:—



Acid ethers are monobasic acids, formed by the direct action of tartaric acid on the respective alcohols; the neutral ethers are formed by passing hydrochloric acid gas into a solution of tartaric acid in an alcohol. Further treating these neutral ethers with chlorides of acid radicles, other neutral ethers are formed, in which one or more of the alcoholic hydrogen-atoms are replaced by acid radicles.* In this manner are formed such compounds as the following:—



The alcoholic hydrogen in these neutral ethers may be replaced by potassium and sodium.

* Perkin, Chem. Soc. Journ. [2], v. 139.

POTASSIUM SALT, WHICH IS VERY SOLUBLE IN WATER.

Inactive tartaric acid is much more soluble in water than tartaric or racemic acid (10 parts of it dissolve in 8 parts of water (59° F.)). It does not deflect the plane of polarization, but racemic acid in not being resolvable into the two active isomers, heated to 170° C. (338° F.), however, it is converted into inactive acid.

HEMOTARTARIC ACID, $C_4H_6O_6 = C_4H_4(OH)_2 \begin{matrix} \swarrow CO_2H \\ \searrow CO_2H \end{matrix}$ of which is known, is formed from dibromopyrotartaric acid.

Rhodizonic Acid, $C_5H_4O_6$.—When potassium is heated with dry carbon monoxide, the latter is absorbed in large quantities in a porous substance generated, which, according to Brodie, is potassium rhodizone. Brought in contact with water it decomposes with great violence; the dry substance occasionally explodes; when anhydrous phosphoric acid is poured upon it, a great elevation of temperature ensues, but the decomposition is far less violent than with water. The product is potassium rhodizonate, which remains as a red powder insoluble in alcohol, but soluble in water with a deep red color. This contains $C_5H_4K_2O_6$.

When solution of potassium rhodizonate is boiled, it becomes yellow from decomposition of the acid, and is then found to contain potash, and a salt of Croconic acid, $C_5H_2O_5$. This acid is isolated; it is yellow, easily crystallizable, soluble both in water and alcohol. It is likewise bibasic.

Citric Acid, $C_6H_8O_7 = C_3H_4(OH)_2(CO_2H)_3$.—This acid is found in large quantities from the juice of lemons; it is found in many fruits, as in gooseberries, currants, etc., in conjunction with sugar. To prepare it, the juice is allowed to ferment a short time, the mucilage and other impurities may separate and subside; they are then carefully saturated with chalk, whereby insoluble calcium citrate is produced. This is thoroughly washed, decomposed by the addition of sulphuric acid diluted with water, and the filtered solution

brought in contact with putrid flesh as a ferment, yields butyric acid and small quantities of succinic acid. It is entirely decomposed when heated with sulphuric and nitric acids: the latter converts it into oxalic acid. Caustic potash, at a high temperature, resolves it into acetic and oxalic acids. The alkaline citrates, treated with chlorine, yield chloroform, together with other products.

Citric acid is tetratomic and tribasic. With *potassium* it forms a neutral salt containing $C_6H_5K_3O_7$, and two acid salts containing respectively $C_6H_6K_2O_7$ and $C_6H_7KO_7$; and similar salts with the other alkali-metals. With dyad metals it chiefly forms salts in which two or three hydrogen-atoms in the molecule $C_6H_8O_7$, are replaced by metals: with *calcium*, for example, it forms the salts $C_6H_6CaO_7 + H_2O$ and $(C_6H_5O_7)_2Ca + H_2O$. With *lead* it forms two salts similar in constitution to the calcium salts, and likewise a tetraplumbic salt containing $(C_6H_2O_7)_2Pb_4.PbH_2O_7$.

The citrates of the *alkali-metals* are soluble, and crystallize with greater or less facility; those of *barium*, *strontium*, *calcium*, *lead*, and *silver* are insoluble.

Citric acid resembles tartaric acid in its relations to ferric oxide, preventing the precipitation of that substance by excess of ammonia. The citrate obtained by dissolving hydrated ferric oxide in solution of citric acid, dries up to a pale-brown, transparent, amorphous mass, which is not very soluble in water; an addition of ammonia increases the solubility. Citrate and ammonio-citrate of iron are used as medicinal preparations.

Citric acid is sometimes adulterated with tartaric acid: the fraud is easily detected by dissolving the acid in a little cold water, and adding to the solution a small quantity of potassium acetate. If tartaric acid be present, a white crystalline precipitate of cream of tartar will be produced on agitation. Citric acid is further distinguished from tartaric acid by the characters of its calcium salt. An aqueous solution of citric acid is not precipitated by lime-water in the cold, but on boiling a precipitate is formed, consisting of trienolic citrate, insoluble in potash-lye. Calcium tartrate, on the other hand, dissolves in alkalis, and is precipitated therefrom as a jelly on boiling.

Citric acid forms ethers in which 1, 2, or 3 hydrogen-atoms are replaced by methyl and other monad alcohol-radicles. The neutral ethers are formed by passing gaseous hydrogen chloride into an alcoholic solution of citric acid. The *trimethylic ether*, $C_3H_4(OH)(CO_2C_2H_5)_3$, is crystalline; the *triethylic ether* boils, with partial decomposition, at about $280^\circ C.$ ($536^\circ F.$).

By treating these neutral ethers with acetyl chloride, the alcoholic hydrogen may also be replaced, and triethylic acetocitrate, $C_3H_4(O.CO_2C_2H_5)_3$, produced, which boils at $288^\circ C.$ ($550.4^\circ F.$). By treating the same ethers with nitric acid, the alcoholic hydrogen may be replaced by NO_2 .

Pentatomic Acids.

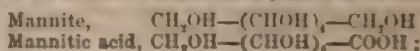
Of these only one is known, viz., the bibasic acid—

Aposorbic acid, $C_5H_6O_7 = C_3H_3(OH)_3 \begin{smallmatrix} < CO_2H \\ < CO_2H \end{smallmatrix}$, which may be regarded as a trioxypyrotartaric acid. It is produced by oxidizing sorbin with nitric acid, and crystallizes in small laminae, easily soluble in water, and melting with decomposition at about $110^\circ C.$ ($230^\circ F.$).

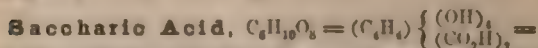
Hexatomic Acids.

Gluconic Acid, $C_6H_{12}O_7 = C_6H_6(OH)_5.CO_2H$, is obtained by oxidizing grape-sugar with chlorine water and removing the chlorine with silver oxide. It is a non-crystallizable syrup, easily soluble in water, and nearly insoluble in alcohol. It is monobasic. Its calcium and barium salts and the ethylic ether crystallize well; the formula of the calcium salt is $(C_6H_{11}O_7)_2Ca + 2H_2O$.

Mannitic Acid, $C_6H_{12}O_7 = C_6H_6(OH)_5.CO_2H$, is produced by oxidation of mannite, $C_6H_{14}O_6$, under the influence of platinum black. It is a gummy mass, soluble in water and in alcohol, insoluble in ether. According to its mode of formation it might be expected to be monobasic:



but from the observations of Gorup-Besanez, who discovered it, it appears to be bibasic, its potassium salt containing $C_6H_{10}KO_7$, and the calcium salt, $C_6H_{10}CaO_7$.



$CO.OH-(CHOH)_4-CO.OH$.—This acid is produced by the action of dilute nitric acid on cane sugar, glucose, milk-sugar, and mannite, and is often formed in the preparation of oxalic acid, being, from its superior solubility, found in the mother liquor from which the oxalic acid has crystallized. It may be made by heating together 1 part of sugar, 2 parts of nitric acid, and 10 parts of water. When the reaction seems terminated, the acid liquid is diluted and neutralized with chalk; the filtered liquid is mixed with lead acetate; and the insoluble lead saccharate is washed, and decomposed by sulphuretted hydrogen. The acid slowly crystallizes from a solution of syrupy consistence in long colorless needles; it has a sour taste, and forms soluble salts with lime and baryta. When mixed with silver nitrate it gives no precipitate, but, on the addition of ammonia, a white insoluble substance separates, which, on gently warming the whole, is reduced to metallic silver, the vessel being lined with a smooth and brilliant coating of the metal. Nitric acid converts saccharic into oxalic and dextrotartaric acids.

There are two *potassium saccharates*, containing $C_6H_7KO_8$ and $C_6H_8K_2O_8$; the *silver-salt* contains $C_6H_7Ag_2O_8$; the *barium, magnesium, zinc, and cadmate salts* have the composition $C_6H_8M''O_8$; and there are two *ethylic ethers*, containing $C_6H_9(C_2H_5)_2O_8$ and $C_6H_8(C_2H_5)_4O_8$. In these compounds saccharic acid appears to be bibasic, as might be expected from its constitution, and mode of formation; the composition of the lead-salts, however, seems to show that it is sexbasic as well as hexatomic, for Heintz has obtained a lead-salt containing $C_6H_4Pb_3O_8$; but the composition of the lead saccharates varies considerably according to the manner in which they are prepared.

Diethylic Saccharate, $C_6H_4(OH)_4 \begin{array}{l} \text{CO}_2.C_2H_5 \\ \text{CO}_2.C_2H_5 \end{array}$, is crystalline, and easily soluble in water. Ammonia converts it into the amide $C_6H_4(OH)_4(CO.NH_2)_2$, which is a white powder. The ether, treated with acetyl chloride, yields the tetracetylic compound $C_6H_4(O.C_2H_3O)_4 \begin{array}{l} \text{CO}_2.C_2H_5 \\ \text{CO}_2.C_2H_5 \end{array}$.

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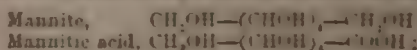
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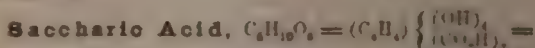
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Mucic Acid, $C_6H_{10}O_8 = C_6H_5(OH)_4(CO_2H)_2$, isomeric with saccharic acid, is produced, together with a small quantity of oxalic acid, by the

action of rather dilute nitric acid on sugar and gum. It may be easily prepared by heating together in a flask or retort, 1 part of milk-sugar or gum, 3 parts of nitric acid, and 1 part of water; the mucic acid is afterwards collected upon a filter, washed and dried. It has a slightly sour taste, and reddens vegetable colors. It requires for solution 66 parts of boiling water. By prolonged boiling with water, it is converted into the isomeric paramucic acid. By boiling with nitric acid it is resolved into oxalic and racemic acids. It is decomposed by heat, yielding, among other products, **pyromucic acid**, $C_8H_6O_8$:



Mucic acid is bibasic, yielding for the most part neutral salts containing $C_8H_8M_2O_8$ and $C_8H_6M''O_8$; with the alkali-metals it also forms acid salts, such as $C_8H_7KO_8$.

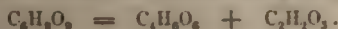
The neutral potassium and ammonium salts crystallize well, and are but slightly soluble in cold water; the acid salts are easily soluble. The neutral ammonium salt is resolved by heat into ammonia, water, and pyrol, C_2H_5N .

Diethylic Mucate, $C_8H_4(OH)_4(CO_2C_2H_5)_2$, obtained by heating mucic acid with alcohol and sulphuric acid, is crystalline, soluble in hot water, melts at $158^\circ C.$ ($316.4^\circ F.$), and is converted by acetyl chloride into the tetra-acetyl compound, $C_8H_4(O.C_2H_5O)_4(CO_2C_2H_5)_2$, which melts at $177^\circ C.$ ($350.6^\circ F.$).

Deoxallic or Racemo-carbonic Acid, $C_8H_6O_8$, probably $= C_8H_4(OH)_4(CO_2H)_2$, is produced by the action of sodium amalgam on ethylic oxalate:



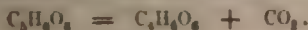
Deoxallic acid is not known in the free state, being resolved, on evaporation of its aqueous solution, into racemic and glyoxylic acids:



The acid is essentially tribasic, its ammonium salt having the composition $C_8H_7(NH_4)_3O_8 + H_2O$; but it also forms salts in which 4 atoms of hydrogen (one alcoholic) are replaced by metal, the silver salt being $C_8H_4Ag_4O_8 + H_2O$, and the barium salt $C_8H_4Ba_2O_8 + 3H_2O$. By the action of acetic acid on its potassium salt it is resolved into acetic acid and Löwig's deoxalic acid, $C_8H_6O_8$:



This last acid, $C_8H_4(OH)_4(CO_2H)_3$, forms large colorless crystals, easily soluble in water and in alcohol. It is tribasic. Heated with water to 100° , it is resolved into racemic acid and carbon dioxide:



Pyromucic Acid and its Derivatives.

Pyromucic Acid, $C_8H_6O_8 = C_8H_5O_7.COOH$, is produced by the dry distillation of mucic acid, or more advantageously by boiling furfural with water and recently precipitated silver oxide; the silver is precipitated by hydrochloric acid, the filtrate evaporated, and the pyromucic acid purified by crystallization from dilute alcohol.

Pyromucic acid crystallizes in colorless laminae or needles, easily soluble

in water, especially if hot, moderately soluble in alcohol. It melts at 134°C . (273.2°F .), and sublimes at 100° . It is monobasic. The silver salt, $\text{C}_6\text{H}_3\text{O}_3\text{Ag}$, crystallizes in laminae; the barium salt, $(\text{C}_6\text{H}_3\text{O}_3)_2\text{Ba}$, forms crystals easily soluble in water. The ethylic ether, $\text{C}_6\text{H}_3\text{O}_3\cdot\text{C}_2\text{H}_5$, obtained by distilling the acid with hydrochloric acid and alcohol, is a crystalline mass, melting at 34°C . (93.2°F .), and boiling at $206\text{--}210^{\circ}\text{C}$. ($401.4\text{--}410^{\circ}\text{F}$.). The chloride, $\text{C}_6\text{H}_3\text{O}_3\cdot\text{COCl}$, produced by distilling pyromucic acid with phosphorus pentachloride, boils at 170°C . (348°F .), and is converted by ammonia into the amide, $\text{C}_6\text{H}_3\text{O}_3\cdot\text{CONH}_2$, a crystalline substance, soluble in water, and melting at 130°C . (266°F .).

Barium pyromucate, distilled with soda-lime, yields tetraphenol, $\text{C}_6\text{H}_3\text{O}$, or $\text{C}_6\text{H}_2\text{O}\cdot\text{OH}$ (4-carbon phenol), as a colorless liquid, boiling at 32°C . (89.6°F .).

Isopyromucic acid, $\text{C}_6\text{H}_3\text{O}_3$, is produced, together with pyromucic acid, by the dry distillation of mucic acid, and may be separated from the latter by solution in a small quantity of cold water. It sublimes below 100° in white laminae, which turn yellow on exposure to the air, melt at 83°C . (179.6°F .), dissolve very easily in water, alcohol, and ether.

Carbopyrrolamide, $\text{C}_4\text{H}_5\text{N}_2\text{O} = \text{C}_4\text{H}_4\text{N}_2\text{CO}\cdot\text{NH}_2$, produced by dry distillation of ammonium pyromucate, forms white shining laminae, easily soluble in alcohol and in ether. It melts at 173°C . (343.4°F .), and does not resolidify till cooled to 133°C . (271.4°F .). By boiling with water it is resolved into ammonia and carbopyrrollic acid :



Carbopyrrollic acid, $\text{C}_4\text{H}_4\text{N}_2\text{CO}\cdot\text{OH}$, crystallizes in small prisms, sublimes at about 190°C . (374°F .), and is decomposed by sudden heating into carbon dioxide and pyrrol :



Barium carbopyrrolate crystallizes in large laminae.

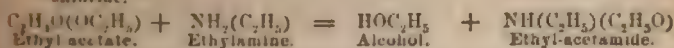
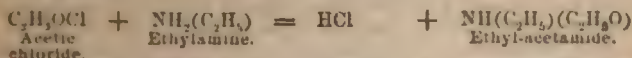
Pyrrol, $\text{C}_4\text{H}_5\text{N}$, is a weak base occurring in coal-tar oil and in bone-oil, and producible by distillation of ammonium pyromucate and of carbopyrrollic acid. It may be prepared from bone-oil by dissolving out the basic constituents with sulphuric acid, and submitting the acid solution to prolonged boiling, whereby the stronger bases are retained, while the pyrrol distils over. The distillate is heated with solid potassium hydroxide, when the pyrrol combines slowly with the alkali, admixed impurities being volatilized. On dissolving the potassium compound in water, the pyrrol separates on the surface as an oily liquid. Pyrrol is colorless, insoluble in water and alkalies, slowly soluble in acids : it has an ethereal odor resembling that of chloroform, a specific gravity = 1.077, and boils at 133°C . (271.4°F .). It is easily recognized by the purple color which it imparts to fir-wood moistened with hydrochloric acid.

By heating an acid solution of pyrrol, a red, flaky substance, *pyrrol-red*, is produced, containing $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}$, the formation of which is represented by the following equation :—

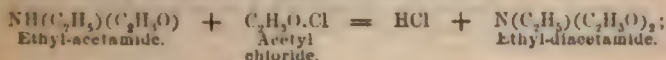


Furfurol, $\text{C}_5\text{H}_4\text{O}_2 = \text{C}_4\text{H}_3\text{O}\cdot\text{COH}$.—This compound, which is the aldehyde of pyromucic acid, is formed in the dry distillation of sugar, and by distilling bran with dilute sulphuric acid or zinc chloride. To prepare it, 1 part of bran is mixed with 1 part of sulphuric acid diluted

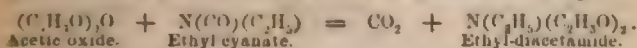
Secondary monamides (alkalamides) containing an acid-radicle and an alcohol-radicle, are formed by processes similar to those above given for the formation of the primary monamides, substituting amines for ammonia; thus:



Tertiary monamides are those in which the whole of the hydrogen in one molecule of ammonia is replaced by acid-radicles or by acid- and alcohol-radicles. Those of the latter kind, called tertiary alkalamides, are produced by the action of acid chlorides on secondary alkalamides:



or by the action of monatomic acid oxides on cyanic ethers; e. g.:

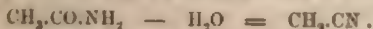


Monamides are for the most part crystalline bodies soluble in alcohol and ether. The lower members of the group are likewise soluble in water, and distil without decomposition. As they contain both a basic group (NH_2), and an acid group, they are capable of acting both as bases and as acids, combining, on the one hand, with acids to form saline compounds, such as $\text{C}_2\text{H}_5\text{O.NH}_2.\text{NO}_2\text{H}$, which, however, are not very stable; and, on the other hand, forming salts by substitution of a metal for one atom of hydrogen, thus *silver-acetamide*, $\text{C}_2\text{H}_5\text{O.NHAg}$, is obtained in crystalline scales, by saturating an aqueous solution of acetamide with silver oxide.

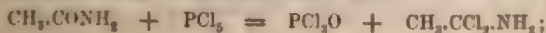
Amides are less stable than amines, the combination of the amidogen-group with acid-radicles ($\text{C}_2\text{H}_5\text{O}$, for example), being weaker than the combination of the same group with hydrocarbons, as in the amines. Consequently they are more easily decomposed than amines, their decomposition being effected by heating with water, or more readily with alkalis:



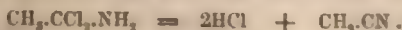
Primary amides heated with *phosphoric anhydride* or *phosphorus trichloride*, give off 1 mol. water, and are converted into nitrils or alcoholic cyanides; e. g., acetamide into methyl cyanide or acetonitril:



When phosphorus pentachloride acts upon an amide, the oxygen-atom of the latter is first replaced by two atoms of chlorine, and the resulting chloride when heated gives up 1 mol. HCl ; thus:



and



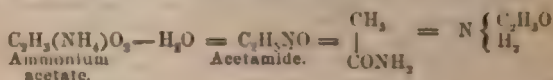
Formamide, $\text{CH}_3\text{NO} = \text{CHO.NH}_2$, the amide of formic acid, is obtained by dry distillation of ammonium formate, or by heating ethyl formate to 100° with alcoholic ammonia. It is a liquid which dissolves easily in water and in alcohol, and boils with partial decomposition at $192^\circ\text{--}195^\circ\text{C}$. ($377.6^\circ\text{--}385^\circ\text{F.}$). When quickly heated, it is resolved into carbon

AMIDES.

We have had frequent occasion to speak of these compounds, as derived from ammonium-salts by abstraction of water, or from acids by substitution of amidogen, NH_2 , for hydroxyl, OH , or from one or more molecules of ammonia by substitution of acid-radicles for hydrogen. They are divided (like amines) into monamides, diamides, and triamides, each of which groups is further subdivided into primary, secondary, and tertiary amides, according as one-third, two-thirds, or the whole of the hydrogen is replaced by acid-radicles. If the hydrogen is replaced partly by acid-radicles, and partly by alcohol-radicles, the compound is called alkalamide; for example, ethylacetamide, $\text{NH}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_5\text{O})$; ethyldiacetamide, $\text{N}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_5\text{O})_2$.

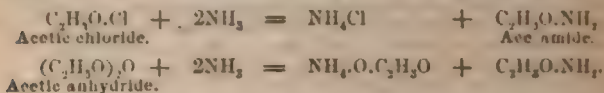
AMIDES DERIVED FROM MONATOMIC ACIDS.

A monatomic acid yields but one primary amide, which may be formed: 1. From its ammonium-salt by direct abstraction of a molecule of water, under the influence of heat; thus:



This method is especially adapted to the preparation of volatile amides.

2. By the action of ammonia on acid chlorides or anhydrides:



This method is especially adapted to the preparation of amides which are insoluble in water.

3. By the action of ammonia on compound ethers:



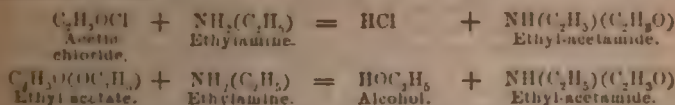
This reaction often takes place at ordinary temperatures, but is for the most part best effected by heating the two bodies together in alcoholic solution.

Secondary monamides are those in which two atoms of hydrogen in a molecule of ammonia are replaced by two univalent or one bivalent acid-radicle, or by one acid-radicle and one alcohol-radicle. Those containing only univalent radicles are formed by the action of dry hydrochloric acid gas on primary monamides at a high temperature; e. g., diacetamide from acetamide:

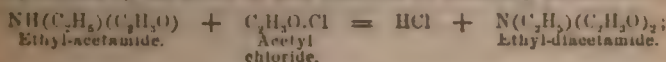


Those containing bivalent acid-radicles are called imides: e. g., succinimide, $\text{NH}(\text{C}_4\text{H}_4\text{O}_2)$. They are derived from dibasic acids, and will be noticed further on.

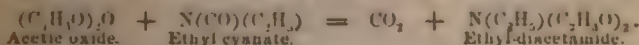
Secondary monamides (alkalamides) containing an acid-radicle and an alcohol-radicle, are formed by processes similar to those above given for the formation of the primary monamides, substituting amines for ammonia; thus:



Tertiary monamides are those in which the whole of the hydrogen in one molecule of ammonia is replaced by acid-radicles or by acid- and alcohol-radicles. Those of the latter kind, called tertiary alkalamides, are produced by the action of acid chlorides on secondary alkalamides:



or by the action of monatomic acid oxides on cyanic ethers; *e. g.*:

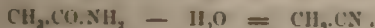


Monamides are for the most part crystalline bodies soluble in alcohol and ether. The lower members of the group are likewise soluble in water, and distil without decomposition. As they contain both a basic group (NH_2), and an acid group, they are capable of acting both as bases and as acids, combining, on the one hand, with acids to form saline compounds, such as $\text{C}_2\text{H}_5\text{O.NH}_2.\text{NO}_2\text{H}$, which, however, are not very stable; and, on the other hand, forming salts by substitution of a metal for one atom of hydrogen; thus *silver-acetamide*, $\text{C}_2\text{H}_5\text{O.NHAg}$, is obtained in crystalline scales, by saturating an aqueous solution of acetamide with silver oxide.

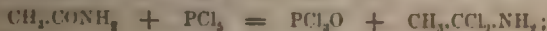
Amides are less stable than amines, the combination of the amidogen-group with acid-radicles ($\text{C}_2\text{H}_5\text{O}$, for example), being weaker than the combination of the same group with hydrocarbons, as in the amines. Consequently they are more easily decomposed than amines, their decomposition being effected by heating with water, or more readily with alkalies:



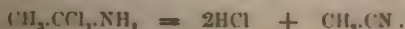
Primary amides heated with *phosphoric anhydride* or *phosphorus trichloride*, give off 1 mol. water, and are converted into nitrils or alcoholic cyanides, *e. g.*, acetamide into methyl cyanide or acetonitril:



When phosphorus pentachloride acts upon an amide, the oxygen-atom of the latter is first replaced by two atoms of chlorine, and the resulting chloride when heated gives up 1 mol. HCl ; thus:



and



Formamide, $\text{CH}_3\text{NO}=\text{CHO.NH}_2$, the amide of formic acid, is obtained by dry distillation of ammonium formate, or by heating ethyl formate to 100° with alcoholic ammonia. It is a liquid which dissolves easily in water and in alcohol, and boils with partial decomposition at 192°C – 195°C . (377.0°F – 385°F). When quickly heated, it is resolved into carbon

monoxide and ammonia. By dehydration with phosphoric anhydride it is converted into hydrogen cyanide or formonitril, HCN .

Acetamide, $\text{C}_2\text{H}_5\text{NO} = \text{C}_2\text{H}_5\text{O.NH}_2$, may be obtained by either of the general reactions above described; also by distilling a mixture of dry sodium acetate and sal-ammoniac in equal numbers of molecules. It crystallizes in long needles, melts at 78°C – 79°C . (172.4 – 174.3°F .), and boils without decomposition at 222°C . (431.6°F .). It dissolves easily in water and in alcohol, and when heated with acids or alkalis it takes up water and is resolved into acetic acid and ammonia. It unites with acids, forming unstable compounds, e. g., $\text{C}_2\text{H}_5\text{NO.HCl}$, and $\text{C}_2\text{H}_5\text{NO.NO}_2\text{H}$. On boiling its aqueous solution with mercuric oxide, the latter is dissolved, and the solution on cooling deposits crystals of mercuracetamide ($\text{C}_2\text{H}_5\text{NO}_2\text{Hg}$).

Chloracetamides may be prepared from the three chloroacetic acids in the same manner as acetamide from acetic acid. Their melting and boiling points are as follows:—

| | | M. P. | B. P. |
|---------------------|---------------------------------------|-------------|---------------------------|
| Monochloracetamide, | $\text{C}_2\text{H}_4\text{ClO.NH}_2$ | 116° | 224° – 225° |
| Dichloracetamide, | $\text{C}_2\text{HCl}_2\text{O.NH}_2$ | 96° | 235° – 236° |
| Trichloracetamide, | $\text{C}_2\text{Cl}_3\text{O.NH}_2$ | 136° | 238° – 239° |

Diacetamide, $\text{NH} < \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{C}_2\text{H}_5\text{O} \end{smallmatrix}$, obtained by heating acetamide in a stream of hydrogen chloride, forms crystals easily soluble in water, melts at 50°C . (138.2°F .), and boils at 210° – 215°C . (410 – 419°F .).

Triacetamide, $(\text{C}_2\text{H}_5\text{O})_3\text{N}$, obtained by heating acetonitril to 260°C . (392°F .) with acetic anhydride, melts at 78° – 79°C . (172.4 – 174.3°F .).

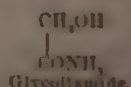
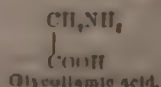
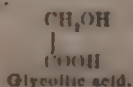
Propionamide, $\text{C}_3\text{H}_7\text{O.NH}_2$, is very much like acetamide, melts at 75° – 76°C . (167 – 168.8°F .), and boils at 210°C . (410°F .).

Butyramide, $\text{C}_4\text{H}_9\text{O.NH}_2$, crystallizes in laminae, melts at 115°C . (239°F .), and boils at 216°C . (420.8°F .).

Isovaleramide, $\text{C}_5\text{H}_9\text{O.NH}_2$, obtained from isovaleric acid, sublimes in laminae which are soluble in water.

AMIDES DERIVED FROM DIATOMIC AND MONOBASIC ACIDS.

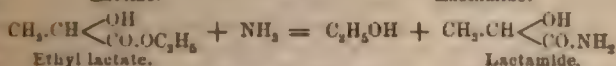
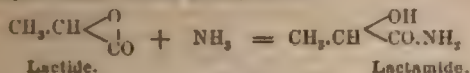
Acids of this group may give rise to two monamides, both formed by substitution of NH_2 for OH , and therefore having the same composition. They are, however, isomeric, not identical, the one formed by replacement of the alcoholic hydroxyl being acid, while the other, formed by replacement of the basic hydroxyl, is neutral. The acid amides thus formed are called amic or amidic acids. Glycollic acid, for example, yields amidoglycollic or glycollamic acid and glycollamide, both containing $\text{C}_2\text{H}_3\text{NO}_2$:



1. Neutral Amides.

These compounds are formed by the action of ammonia in the gaseous

state or in alcoholic solution on the corresponding oxides or anhydrides, or on the ethylic ethers of the acids; thus:



Glycollamide, $\text{C}_2\text{H}_5\text{NO}_2 = \text{CH}_2 \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{CO.NH}_2 \end{array}$, is formed by heating

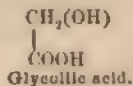
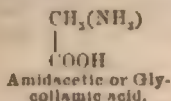
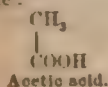
glycollide, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CO} \end{array} \text{O}$, with dry ammonia, and by heating acid ammonium tartrate (p. 758) to 150°C . (302°F .); $\text{C}_2\text{H}_2(\text{NH}_4)_2\text{O}_4 = \text{C}_2\text{H}_5\text{NO}_2 + \text{CO}_2 + \text{H}_2\text{O}$. It crystallizes in needles having a sweetish taste, easily soluble in water, sparingly in alcohol, melting at 100° . By boiling with alkalis, it is resolved into glycollic acid and ammonia.

Lactamide, $\text{C}_3\text{H}_7\text{NO}_2 = \text{CH}_3\text{CH} \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{CO.NH}_2 \end{array}$, obtained as above mentioned, forms crystals easily soluble in water, melting at 74°C . (165.2°F .), resolved by boiling with alkalis into lactic acid and ammonia.

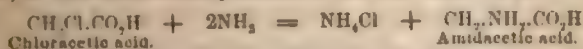
Lactimide. $\text{C}_3\text{H}_5\text{NO} = \text{CH} - \text{CH} \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{NH}_2 \end{array}$, produced by heating alanine, $\text{CH}_3\text{CH} \begin{array}{c} \diagup \text{NH}_2 \\ \diagdown \text{CO.OH} \end{array}$, to 180° – 200°C . (356° – 392°F .) in a stream of hydrogen chloride, forms colorless laminæ or needles, easily soluble in water and in alcohol, melting at 275°C . (527°F .).

2. Amic or Amidic Acids.

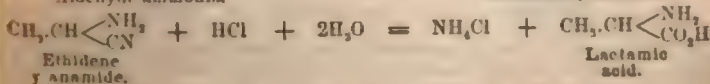
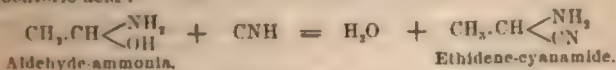
The amic acids of this group are identical with the amidated acids derived from the corresponding monatomic acids, $\text{C}_n\text{H}_{2n}\text{O}_n$, by substitution of amidegen for hydrogen; thus glycollamic acid is identical with amidacetic acid, lactamic with amidopropionic; leucamic with amidocaproic acid; for example:



They are formed: 1. By the action of ammonia on the monochloro-, bromo-, or iodo substitution-products of the fatty acids: *e. g.*,



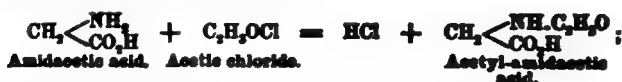
2. By heating the ammonia-compounds of the aldehydes with hydrocyanic and hydrochloric acid, whereby cyanides are produced in the first instance, and afterwards transformed into amido-acids by the action of the hydrochloric acid:



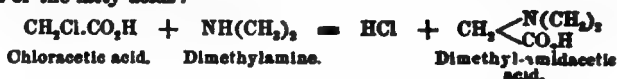
Several of them occur in the animal organism.

These *amino acids* are distinguished from the *isomeric neutral amides* by the more intimate state of combination of their *amidogen-group*, which cannot be separated by boiling with alkalis. As they contain both a *carboxyl group* and an *amidogen group*, they possess both *acid* and *basic* properties, and form *saline compounds* both with *acids* and with *bases*, the *basic* character, however, predominating. Hence, they are often designated by names ending in *ine*, the ordinary termination for *organic bases*, *glycollamic acid* being designated as *glycoccine*, *lactic acid* as *alanine*, *leucamic acid* as *leucine*, etc. They are also designated, as a group, by the name *Alanines*.

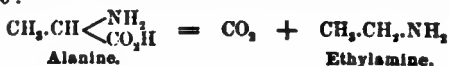
The hydrogen of the *carboxyl group* in these compounds may be replaced by *alcohol-radicles*, yielding *compound ethers*, which, however, are somewhat unstable; that of the *amidogen group* may be replaced by *alcohol-radicles* or by *acid-radicles*. The *acid derivatives* are obtained by treating the *amido-acids*, or their *ethers*, with the *haloid compounds of acid-radicles*:



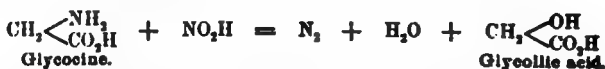
the *alcoholic derivatives* by the action of *amines* on *substitution-derivatives of the fatty acids*:



The *alanines* are *crystalline bodies*, mostly having a *sweetish taste*, easily soluble in *water*, insoluble for the most part in *alcohol* and *ether*. They have a *neutral reaction*, and, as already observed, are not decomposed by boiling with *alkalies*, but when fused with *alkaline hydrates*, they are decomposed into *ammonia* and *fatty acids*. By *dry distillation*, especially in contact with *baryta*, they are resolved into *amines* and *carbon dioxide*:



Nitrous acid converts them into *oxyacid*:



Amidoacetic Acid, or Glycoccine, $\text{C}_2\text{H}_5\text{NO}_2 = \text{CH}_3\text{CH} \begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{CO}_2\text{H} \end{array}$, also called *amidoglycollic acid*, *glycollamic acid*, and *glycoll*, is formed by the action of *ammonia* on *bromoacetic* or *chloroacetic acid*:



also, by the action of *acids* or *alkalies* upon *animal substances*, such as *glue*, *hippuric acid*, *glycollic acid*, etc. From *hippuric acid* it is formed, together with *benzoic acid*, according to the equation:



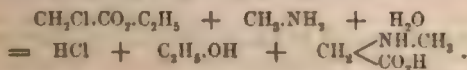
Glycoccine crystallises from *water* in large, hard, transparent, *rhombic prisms*, having a *sweetish taste*, soluble in 4 parts of cold *water*, insoluble in *alcohol* and *ether*. It melts at 170°C . (338°F .), and decomposes at a

higher temperature. By heating with baryta it is resolved into carbon dioxide and methylamine; by treatment with nitrous acid it is converted into glycollic acid. It combines with acids in different proportions. With sulphuric acid it forms the compound $(C_2H_5NO_2)_2SO_4H_2$; and on addition of alcohol to a solution of this sulphate, a salt crystallizing in rectangular prisms is deposited, containing $3C_2H_5NO_2 \cdot SO_4H_2$. It also forms the *hydrochlorides*, $C_2H_5NO_2 \cdot HCl$ and $C_2H_5NO_2 \cdot 2HCl$, the latter of which crystallizes in long prisms. The *nitrate*, $C_2H_5NO_2 \cdot NO_3H$, forms large prisms.

Glycoccine also forms saline compounds by substitution of metals for hydrogen; thus it dissolves *cupric oxide*, forming the salt, $(C_2H_5NO_2)_2Cu + H_2O$, which crystallizes from the hot solution in dark blue needles. The *silver salt*, $C_2H_5NO_2 \cdot Ag$, crystallizes over sulphuric acid. Glycoccine also unites with *metallic salts*, forming crystalline compounds, such as $C_2H_5NO_2 \cdot NO_3K$, and $C_2H_5NO_2 \cdot NO_3Ag$.

The ethylic ether of glycoccine, or *ethyl amidacetate*, $CH_2 < \begin{smallmatrix} NH_2 \\ CO_2C_2H_5 \end{smallmatrix}$, is produced by the action of silver oxide on the hydriodide obtained by heating glycoccine with ethyl iodide in alcoholic solution. It is resolved by evaporation of its aqueous solution into glycoccine and alcohol.

Methyl-glycoccine or *Sarcosine*, $C_3H_7NO_2 = CH_2 < \begin{smallmatrix} NH \cdot CH_3 \\ CO_2H \end{smallmatrix}$, is formed by digesting ethyl chloracetate with excess of a concentrated aqueous solution of methylamine:



The same compound is formed by boiling creatine with baryta-water. The creatine splits into sarcosine and urea, the latter being further decomposed into ammonia and carbonic acid. Sarcosine crystallizes in colorless rhombic prisms, easily soluble in water; it is difficultly soluble in alcohol, insoluble in ether, and has no action upon vegetable colors. It combines with acids to form soluble salts, which have an acid reaction. The double salt of sarcosine with platinum tetrachloride crystallizes in large yellow octohedrons having the composition $2C_3H_7NO_2 \cdot 2HCl \cdot PtCl_4 + 2Aq$. Sarcosine ignited with soda-lime gives off methylamine.

Trimethyl-glycoccine or *Betaine*, $C_5H_{11}NO_2 = CH_2 < \begin{smallmatrix} N(CH_3)_3 \\ CO > O \end{smallmatrix}$,

which exists ready-formed in beet-juice, and is produced by oxidation of choline hydrochloride, and synthetically by heating trimethylamine with monochloroacetic acid, has been already described (p. 646).

Ethyl-glycoccine, $C_4H_9NO_2 = CH_2 < \begin{smallmatrix} NH \cdot C_2H_5 \\ CO_2H \end{smallmatrix}$, obtained by heating chloroacetic acid with ethylamine, forms deliquescent laminæ; it unites with acids, bases, and salts.

Diethyl-glycoccine, $C_6H_{13}NO_2 = CH_2 < \begin{smallmatrix} N(C_2H_5)_2 \\ CO_2H \end{smallmatrix}$, prepared from chloroacetic acid and diethylamine, forms deliquescent crystals, and sublimes below 100° .

Acetyl-glycoccine, or *Aceturic acid*, $CH_2 < \begin{smallmatrix} NH \cdot C_2H_5O \\ CO_2H \end{smallmatrix}$, produced by the action of acetyl chloride on silver-glycoccine, or of acetamide on monochloroacetic acid, crystallizes in small needles, easily soluble in water

and in alcohol, and turning brown at 130°C . (266°F .); reacts like monobasic acid.

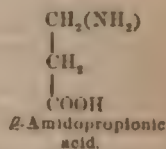
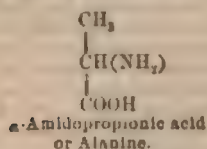
DIGLYCOLLAMIC and TRIGLYCOLLAMIC ACIDS.—Glycocine or glycollamic acid may be regarded as ammonia having one atom of hydrogen replaced by the univalent group $\text{CH}_2\text{CO}_2\text{H}$, and the similar replacement of 2 and 3 hydrogen-atoms in ammonia may give rise to di- and tri-glycollamic acids.

| | | | | |
|---|---|---|---|----------------------|
| $\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$ | . | . | . | Glycollamic acid. |
| $\text{NH}(\text{CH}_2\text{CO}_2\text{H})_2$ | . | . | . | Diglycollamic acid. |
| $\text{N}(\text{CH}_2\text{CO}_2\text{H})_3$ | . | . | . | Triglycollamic acid. |

These three acids are produced simultaneously by boiling monochloroacetic acid with strong aqueous ammonia; and on concentrating the resulting solution, filtering from separated sal-ammoniac, boiling the filtrate with lead oxide, and filtering again, the filtrate on cooling deposits the lead salt of triglycollamic acid, while the lead salts of the other two acids remain in solution. To separate the diglycollamic acid, the lead is precipitated by hydrogen sulphide, and the filtered solution boiled with zinc carbonate, whereupon the sparingly soluble zinc diglycollamate separates out, while the zinc-salt of glycocine remains in solution.

Diglycollamic and triglycollamic acids are crystalline bodies which form salts both with acids and with bases; the former is bibasic, the latter tribasic.

Amidopropionic Acids, $\text{C}_3\text{H}_7\text{NO}_2 = \text{C}_3\text{H}_5(\text{NH}_2)\text{O}_2$.—Of these there are two modifications, analogous to the two bromo-, chloro-, and iodo-propionic acids, viz.:—



Alanine is produced by the action of alcoholic ammonia on α -chloro- or α -bromo-propionic acid, or by heating aldehyde ammonia with hydrocyanic and hydrochloric acids, the reactions being precisely similar to those by which glycocine is obtained from the corresponding derivative of acetic acid. It crystallizes in tufts of hard needles, dissolves in 5 parts of cold water, less easily in alcohol, and is insoluble in ether. When slowly heated, it melts and sublimes undecomposed; but when quickly heated, it is resolved into carbon dioxide and ethylamine. Nitrous acid converts it into lactic acid.

Alanine unites with acids, bases, and salts. The platinum salt $2(\text{C}_3\text{H}_7\text{NO}_2\cdot\text{HCl})\cdot\text{PtCl}_6$ crystallizes in large reddish prisms.

β -Amidopropionic acid, $\text{CH}_2(\text{NH}_2)\text{CH}_2\text{CO}_2\text{H}$, prepared by the action of ammonia on β -iodopropionic acid, forms rhombic prisms easily soluble in water, and sublimes with partial decomposition when heated. Its compound is much more soluble than that of the α -acid.

α -Amidobutyric Acid, $\text{C}_4\text{H}_9\text{NO}_2 = \text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, called *Propanine*, is prepared from α -bromobutyric acid. It crystallizes in small laminæ or needles, easily soluble in water.

Amidisovaleric Acid, $C_6H_{11}NO_2 = \begin{array}{c} CH(CH_3)_2 \\ | \\ CH < \begin{array}{l} NH_2 \\ CO_2H \end{array} \end{array}$, occurs in the pancreas of the ox, and is formed artificially by the action of ammonia on isovaleric acid. It crystallizes in shining prisms, sublimates without previous fusion, dissolves in water and alcohol, but less easily than leucine.

Amidocaproic Acid or Leucine, $C_6H_{13}NO_2 = C_5H_{10} < \begin{array}{l} NH_2 \\ CO_2H \end{array}$, is formed by the action of ammonia on bromocaproic acid, and by digesting ferrous-ammonia with hydrocyanic and hydrochloric acids:



Leucine is also formed by the decomposition of animal substances, such as glue, horn, wool, etc., during putrefaction, and by the treatment of these substances with acids or alkalies. It was first discovered in putrid urine; more recently it has been found in several parts of the animal organism.

Leucine crystallizes in white shining scales, which melt at 100° , and may be sublimed without decomposition; it is but little soluble in water, less in alcohol, insoluble in ether. When heated with caustic baryta, it splits into carbon dioxide and amylamine: $C_6H_{13}NO_2 = C_5H_{13}N + CO_2$. It unites with acids, bases, and salts. Treatment with nitrous acid converts it into leucic acid, $C_6H_{13}O_3$.

AMIDES DERIVED FROM DIATOMIC AND BIBASIC ACIDS, $C_nH_{2n} < \begin{array}{l} CO_2H \\ CO_2H \end{array}$.

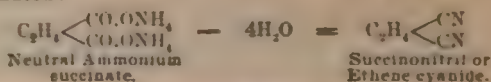
Each acid of this group may give rise to three amides, viz.: 1. An acid amide or amic acid, derived from the acid ammonium salt by abstraction of one molecule of water. 2. A neutral monamide, or imide, derived from the same salt by abstraction of $2H_2O$. 3. A neutral amide, or diamide, derived from the neutral ammonium salt by abstraction of $2H_2O$; thus from succinic acid, $C_2H_4(CO_2H)_2$, are derived:

1. Succinamic acid, $C_2H_4 < \begin{array}{l} CO.NH_2 \\ CO.OH \end{array} = C_2H_4 < \begin{array}{l} CO.ONH_4 \\ CO.OH \end{array} - H_2O$
Acid Ammonium succinate.
2. Succinimide. $C_2H_4 < \begin{array}{l} CO \\ CO \end{array} > NH = C_2H_4 < \begin{array}{l} CO.ONH_4 \\ CO.OH \end{array} - 2H_2O$
Acid Ammonium succinate.
3. Succinamide. $C_2H_4 < \begin{array}{l} CO.NH_2 \\ CO.NH_2 \end{array} = C_2H_4 < \begin{array}{l} CO.ONH_4 \\ CO.ONH_4 \end{array} - 2H_2O$
Neutral Ammonium succinate.

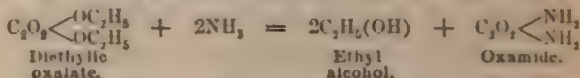
The two neutral amides may also be regarded as derived from one or two molecules of ammonia by substitution of the diatomic radical of the acid (two atoms of hydrogen, and the amic acid by similar substitution in a compound molecule, $NH_2.HHO$:



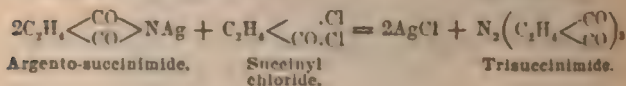
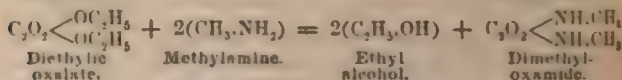
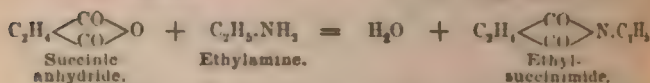
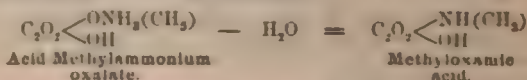
By abstraction of four molecules of water from the neutral ammonium salts, nitrils or cyanides of the corresponding diamine alcohol-radicles are produced:



The amic acids of this group are also formed by boiling the imides with water: thus succinimide, $\text{C}_4\text{H}_5\text{NO}_2$, by taking up H_2O is converted into succinamic acid, $\text{C}_4\text{H}_7\text{NO}_3$; and the neutral amides are formed by shaking up the corresponding neutral ethers with aqueous ammonia: e. g.,



The type or extra-radicle hydrogen in these amides may be replaced by alcoholic or by acid radicles, thereby producing alkalamides, secondary and tertiary diamides, etc. The modes of producing such compounds may be understood from the following equations:



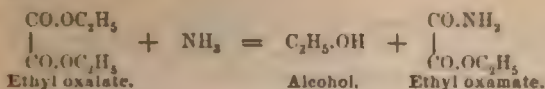
Amides of Oxalic Acid

Oxamic Acid, $\text{C}_2\text{H}_3\text{NO}_3 = \begin{array}{c} \text{CO.NH}_2 \\ \text{CO.OH} \end{array}$, is produced by heating acid

ammonium oxalate to about 230°C . (446°F .); also as an ammonium-salt by boiling oxamide with aqueous ammonia: $\text{C}_2\text{H}_4\text{N}_2\text{O}_2 + \text{H}_2\text{O} = \text{C}_2\text{H}_2(\text{NH}_2)_2\text{NO}_2$. Oxamic acid is a white crystalline powder sparingly soluble in cold water, still less soluble in alcohol and ether. It is monobasic, and forms numerous crystalline metallic salts.

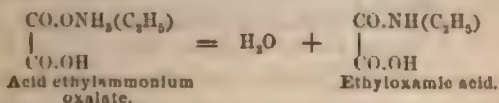
Oxamic ethers may be formed by substitution of alcohol-radicles for hydrogen, either in the group NH_2 or in the group OH of oxamic acid, the resulting ethers being acid in the former case, neutral in the latter. The neutral ethers, also called oxamethanes, are formed by the action

of ammonia, in the gaseous state or in alcoholic solution, on neutral oxalic ethers; thus:



They are crystalline bodies soluble in alcohol, decomposed by boiling water, yielding ammonium oxalate and the corresponding alcohol.

The acid ethers of oxamic acid containing one equivalent of alcohol-radicle, are produced by dehydration of the acid oxalates of the corresponding amines; thus:



Methyloxamic and phenyloxamic acids are also known. These acid ethers are metameric with the neutral oxamic ethers containing the same alcohol-radicles.

The replacement of both the hydrogen-atoms in the group NH_2 in oxamic acid, would also yield monobasic acid ethers; none of these are, however, known in the free state, but the ethylic ethers of dimethyl- and diethyl-oxamic acids have been obtained, *e. g.*, *ethylic-dimethyl-oxamate*, $(\text{C}_2\text{O}_2)_2\text{N}(\text{CH}_3)_2(\text{OC}_2\text{H}_5)$.

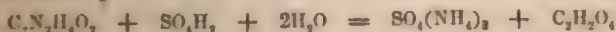
Oxamide, $\text{N}_2\text{H}_4(\text{C}_2\text{O}_2) = \begin{array}{c} \text{CO.NH}_2 \\ | \\ \text{CO.NH}_2 \end{array}$.—This compound is formed by the

action of heat on neutral ammonium oxalate, but is more advantageously prepared by the action of ammonia on neutral ethyl oxalate. It is also formed in several reactions from cyanogen and cyanides; an aqueous solution of hydrocyanic acid, mixed with hydrogen dioxide, yields a crystalline deposit of oxamide: $2\text{CNH} + \text{H}_2\text{O}_2 = \text{C}_2\text{N}_2\text{H}_4\text{O}_2$.

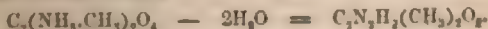
Oxamide is a white, light, tasteless powder, insoluble in cold water, slightly soluble in boiling water, insoluble in alcohol. Heated in an open tube it volatilizes and forms a crystalline sublimate; but its vapor, passed through a red-hot tube, is completely resolved into carbon monoxide, ammonium carbonate, hydrocyanic acid, and urea (carbamide):



Dilute mineral acids decompose it, yielding an ammonium-salt and free oxalic acid; *e. g.*,



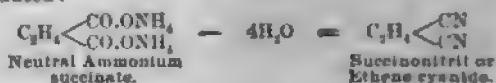
Dimethyloramide, $\text{N}_2(\text{C}_2\text{O}_2)\text{H}_2(\text{CH}_3)_2$, is produced by the dry distillation of methylammonium oxalate:



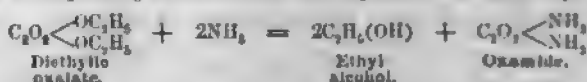
Diethyloxamide and diamyloxamide are obtained in a similar manner.

The imide of oxalic acid is not known; its nitril is dicyanogen, C_2N_2 .

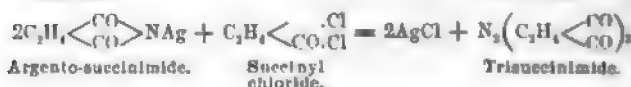
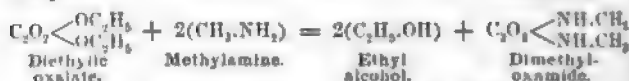
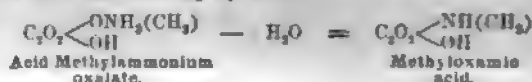
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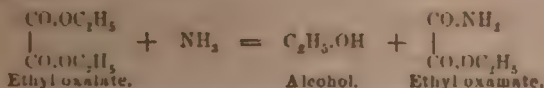
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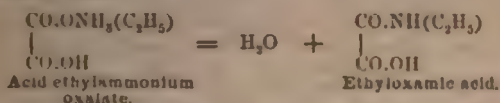
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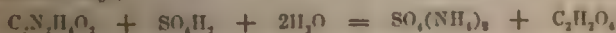
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Oxamide is a white, light, tasteless powder, insoluble in cold water, slightly soluble in boiling water, insoluble in alcohol. Heated in an open tube it volatilizes and forms a crystalline sublimate; but its vapor, passed through a red-hot tube, is completely resolved into carbon monoxide, ammonium carbonate, hydrocyanic acid, and urea (carbamide):



Dilute mineral acids decompose it, yielding an ammonium-salt and free oxalic acid; *e. g.*,



Dimethyluramide, $\text{N}_2(\text{C}_2\text{O}_2)\text{H}_2(\text{CH}_3)_2$, is produced by the dry distillation of methylammonium oxalate:



Diethyloxamide and diamyloxamide are obtained in a similar manner. The imide of oxalic acid is not known; its nitril is dicyanogen, C_2N_2 .

Amides of Succinic Acid.

Succinamic acid, $C_4H_5\begin{matrix} \diagup CO.NH_2 \\ \diagdown CO.OH \end{matrix}$, formed by heating succinimide with baryta-water, is crystalline, and is easily resolved by the action of alkalis into succinic acid and ammonia.

Succinimide, $C_4H_5\begin{matrix} \diagup CO \\ \diagdown CO \end{matrix}NH$, formed by heating succinic anhydride in a stream of dry ammonia, or by distillation of acid ammonium succinate, crystallizes in rhombic plates containing one molecule of water, dissolves easily in water and in alcohol, melts at $126^\circ C.$ ($258.8^\circ F.$), and boils at $288^\circ C.$ ($550.4^\circ F.$).

A hot alcoholic solution of succinimide mixed with a little ammonia and then with silver nitrate, yields on cooling, large crystals of argentic succinimide, $C_4H_5\begin{matrix} \diagup CO \\ \diagdown CO \end{matrix}NAg$; and the solution of this salt in a small quantity of ammonia leaves, on spontaneous evaporation, a syrupy liquid, which gradually solidifies to a mass of hard, brittle crystals of argentammonium-succinimide, $C_4H_5\begin{matrix} \diagup CO \\ \diagdown CO \end{matrix}N(NH,Ag)$.

The acid character of succinimide exhibited in these salts is likewise shown by other imides, the group NH , when associated with CO (as in cyanic acid, $CO \equiv NH$) or with C_2O_3 , as in the salts above described, being capable of exchanging its hydrogen for metals, like the group OH in acids.

Succinamide, $C_4H_7(CO.NH_2)_2$, separates as a white powder when neutral ammonium succinate is shaken up with aqueous ammonia. It is insoluble in cold water and alcohol, but dissolves in hot water, and separates therefrom in slender needles. At $200^\circ C.$ ($392^\circ F.$), it is resolved into ammonia and succinamide.

Amides of Carbonic Acid.

Carbamic Acid, $CO\begin{matrix} \diagup NH_2 \\ \diagdown OH \end{matrix}$, is not known in the free state, that is, as a hydrogen salt, but its ammonium salt, $(CO)(NH_2)(ONH_4)$, enters into the composition of commercial carbonate of ammonia, and is produced, as already noticed (p. 313), by the direct combination of carbon dioxide and ammonia-gas. This salt is easily obtained pure and in large quantity by passing the two gases, both perfectly dry, into cold absolute alcohol, separating the copious crystalline precipitate by filtration from the greater part of the liquid, and heating it with absolute alcohol in a sealed tube to 100° , or above.* The liquid, on cooling, deposits ammonium carbamate in large crystalline laminae, which, if perfectly dried over oil of vitriol, and then heated in a sealed tube to 130° – $140^\circ C.$ (266° – $284^\circ F.$), split up into ammonium carbonate and carbamide, one molecule of it giving up a molecule of water to another:—

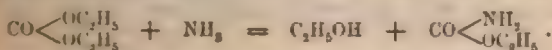


* Kolbe and Basaroff, Chem. Soc. Journal [3], vi. 194.

CARBAMIC ETHERS.—Carbamic acid forms acid and neutral ethers, according as an atom of hydrogen in the group NH_2 or OH is replaced by an alcohol-radicale.

Ethylcarbamic acid, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{C}_2\text{H}_5 \\ \text{OH} \end{smallmatrix}$, is not known in the free state, but its ethylammonium salt, $(\text{CO}) \cdot \text{NH}(\text{C}_2\text{H}_5) \cdot \text{ONH}_2(\text{C}_2\text{H}_5)$, is produced, as a white powder, by passing carbon dioxide into anhydrous ethylamine and by a freezing mixture. Its aqueous solution, like that of ammonium carbonate, does not precipitate barium chloride unless aided by heat. The ethylammonium salt of methylcarbamic acid is obtained in a similar manner.

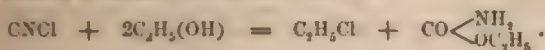
Neutral carbamic ethers are called urethanes. *Ethyl carbamate*, or simply *urethane*, is produced: 1. By leaving ethyl carbonate in contact with aqueous ammonia:—



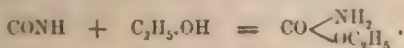
By the action of ammonia on ethyl chlorocarbonate (alcohol saturated with phosgene):—



By passing cyanogen chloride into alcohol:—



By direct union of cyanic acid with alcohol:—

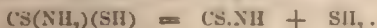


The compound crystallizes in large tables, melts somewhat below 100° , at 180°C. (356°F.); dissolves easily in water, alcohol, and ether. It is decomposed by alkalis into carbon dioxide, ammonia, and alcohol, and by ammonia into alcohol and carbamide:—

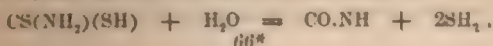


Other urethanes homologous with ethyl carbonate, are obtained by similar reactions, and exhibit similar properties and decompositions. The *isopentyl*-compound, $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{OC}_4\text{H}_9 \end{smallmatrix}$, forms tabular crystals, melts at 52°C. (125°F.), and boils at 177°C. (350.6°F.). The *isopentyl*-compound, $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{OC}_4\text{H}_9 \end{smallmatrix}$, crystallizes from hot water in needles having a metallic lustre, melts at 66°C. (150.8°F.), and boils at 220°C. (428°F.).

Thiocarbamic Acid, $\text{CS} \begin{smallmatrix} \text{NH}_2 \\ \text{SH} \end{smallmatrix}$, is obtained by decomposing its ammonium salt with dilute sulphuric acid, as a reddish oil, which easily splits into thiocyanic acid and hydrogen sulphide:—

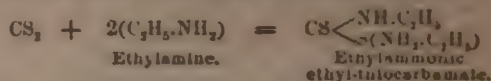


In water it yields cyanic acid and hydrogen sulphide:—



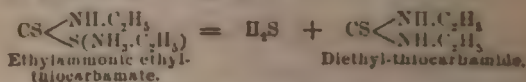
its ammonium salt, $\text{CS}(\text{NH}_2)(\text{S.NH}_2)$, formed by the action of alcoholic ammonia on CS_2 , crystallizes in yellowish needles or prisms.

Acid thiocarbamic ethers, or rather their amine salts, are formed by heating carbon disulphide with amines in alcoholic solution:—

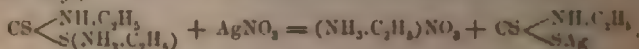


On heating this salt with caustic soda, ethylamine is separated, and an ethyl-thiocarbamate, $\text{CS} \begin{array}{c} \text{NH.C}_2\text{H}_5 \\ \text{SNa} \end{array}$, is produced, from which by

dichloric acid separates ethyl-thiocarbamic acid, $\text{CS} \begin{array}{c} \text{NH.C}_2\text{H}_5 \\ \text{SH} \end{array}$, as an oil which solidifies to a crystalline mass on cooling. By heating the amine salts of ethyl thiocarbamic acid to 100° , alcoholic thiocarbamides are produced (p. 793), e. g.,



By heating the same amine-salts with metallic salts, as silver nitrate, mercuric chloride, salts of ethyl-thiocarbamic acid are precipitated: e. g.,



and these salts, when boiled with water, yield thiocarbimides:



Carbimide, CO: NH or $\text{N} \begin{array}{c} \text{CO} \\ \text{H} \end{array}$, is the same as cyanic acid, and many of the reactions of cyanic acid are most appropriately represented by the formula just given, especially its resolution into carbon dioxide and ammonia under the influence of acids or alkalies:



and the corresponding formation of ethylamine and its homologues by distilling isocyanic ethers (alcoholic carbimides) with potash (p. 542).

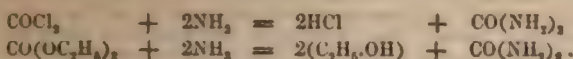
In like manner thiocyanic acid or sulphocyanic acid, CSNH_2 , is identical with thiocarbimide, CS-NH , and the isothiocyanic ethers with alcohol thiocarbimides; allyl isothiocyanate or volatile oil of mustard, for example, is the same as allyl-thiocarbimide, $\text{CS.N.C}_3\text{H}_5$ (see *Thioesters*, p. 546).

Carbamide or **Urea**, $\text{CON}_2\text{H}_4 = \text{CO} \begin{array}{c} \text{NH}_2 \\ \text{NH}_2 \end{array}$.—This compound occurs abundantly in the urine of mammals, and in smaller quantities that of birds and of some reptiles, also in other animal secretions. It is produced artificially: 1. By a transposition of the constituent atoms of ammonium isocyanate, which takes place when its aqueous solution is evaporated:

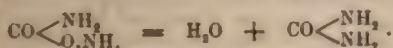


This transformation, discovered by Wöhler in 1828, was the first instance of the artificial formation of a product of the living organism (p. 469).

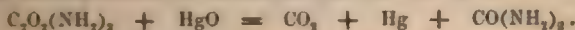
2. By the action of ammonia on carbonyl chloride, or on ethylic carbonate:



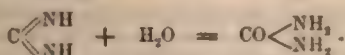
3. By heating ammonium carbamate to 130° – 140° :



4. By heating oxamide with mercuric oxide:



5. By the action of small quantities of acids on cyanamide:



It is also produced by the action of alkalis on creatine and allantoin, and by oxidation of uric acid, guanine, and xanthine.

Preparation.—1. From urine. Fresh human urine is concentrated in water-bath, until reduced to an eighth or a tenth of its original volume, and filtered through cloth from the insoluble deposit of urates and phosphates. The liquid is mixed with about an equal quantity of strong solution of oxalic acid in hot water, and the whole vigorously agitated and left to cool. A very copious fawn-colored crystalline precipitate of *urea oxalate* is thus obtained, which may be placed upon a cloth filter, slightly washed with cold water, and pressed. This is to be dissolved in boiling water, and powdered chalk added until effervescence ceases, and the liquid becomes neutral. The solution of urea is filtered from the insoluble calcium oxalate, warmed with a little animal charcoal, again filtered, and concentrated by evaporation, avoiding ebullition, until crystals form on cooling: these are purified by a repetition of the last part of the process. Another process consists in precipitating the evaporated urine with concentrated nitric acid, when *urea nitrate* is precipitated, which is purified by recrystallization with the aid of animal charcoal, and, lastly, decomposed by barium carbonate, whereby a mixture of barium nitrate and urea is formed, which is to be evaporated to dryness on the water-bath, and exhausted with hot alcohol; the urea then crystallizes on cooling. Urea may also be extracted in great abundance from the urine of horses and cattle duly concentrated, and from which the hippuric acid has been separated by addition of hydrochloric acid; oxalic acid then throws down oxalate in such quantity as to render the whole semi-solid.

2. From ammonium isocyanate.—Potassium isocyanate is dissolved in a small quantity of water, and a quantity of dry neutral ammonium sulphate, equal in weight to the cyanate, is added. The whole is evaporated to dryness in a water-bath, and the dry residue boiled with strong alcohol, which dissolves out the urea, leaving the potassium sulphate and the excess of ammonium sulphate untouched. The filtered solution, concentrated by distilling off a portion of the spirit, deposits the urea in beautiful crystals of considerable size. According to J. Williams,* cyanate of lead is more convenient for this preparation than the potassium salt. It is to be digested at a gentle heat in a sufficient quantity of water with an equivalent quantity of ammonium sulphate, and the liquid filtered and evaporated.

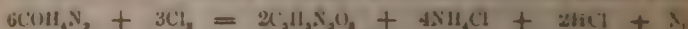
* Chem. Soc. Journal (1868), xxi. 63.

Urea forms transparent, colorless, four-sided prisms, which are efflorescent, soluble in an equal weight of cold water, and in a much smaller quantity at a high temperature. It is also readily dissolved by acids. It is inodorous, has a cooling saline taste, and is permanent in moderate dry air. When heated it melts, and at a higher temperature decomposes, giving off ammonia and ammonium cyanate, and leaving cyanuric acid, which bears a much greater heat without change. The solution of urea is neutral to test-paper; it is not decomposed in the cold by alkalis or calcium hydrate, but at a boiling heat emits ammonia, and forms a metastable carbonate. The same change is produced by fusion with the alkaline hydrates, and when urea is heated with water in a sealed tube to a temperature above 100° :



Urea, heated with a large excess of potassium permanganate, in presence of much free alkali, gives off all its nitrogen in the free state, differing in this respect, from most amides, the nitrogen of which is oxidized by the treatment to nitric acid.

Urea is instantly decomposed by *nitrous acid* into carbon dioxide, nitrogen, and water: $\text{COH}_2\text{N}_2 + 2\text{NO}_2\text{H} = \text{CO}_2 + 2\text{N}_2 + 3\text{H}_2\text{O}$, this decomposition explains the use of urea in preparing nitric ether (p. 573). When *chlorine gas* is passed over melted urea, hydrochloric acid and nitrogen are evolved, and there remains a mixture of sal-ammoniac and cyanuric acid:



A solution of pure urea shows no tendency to change by keeping, and is not decomposed by boiling; in the urine, on the other hand, when it is associated with putrescible organic matter, as mucus, the case is different. In putrid urine no urea can be found, but enough ammonium carbonate to cause brisk effervescence with an acid, and if urine, in a recent state, is long boiled, it gives off ammonia and carbonic acid from the same source.

COMPOUNDS OF UREA.—1. With Acids.—Urea, like glycocine, unites with acids, bases, and salts, but though a diamide, it combines with only one molecule of an acid, one of its amidogen groups being neutralized by the CO-group.

The *nitrate*, $\text{CH}_4\text{N}_2\text{O}.\text{NO}_2\text{H}$, is readily soluble in water, and crystallizes from the aqueous solution in long prisms, but slightly soluble in concentrated acid, and is therefore precipitated by nitric acid from the aqueous solution of urea. The *oxalate*, $(\text{CH}_4\text{N}_2\text{O})_2.\text{C}_2\text{H}_2\text{O}_4$, is obtained as a white crystalline precipitate by mixing the aqueous solutions of oxalic acid and urea, it is but slightly soluble in water.

2. With Metallic Oxides.—On adding moist *silver oxide* to a solution of urea, the compound, $\text{COH}_2\text{N}_2.3\text{Ag}_2\text{O}$, is deposited as a gray powder made up of fine needles. *Mercuric nitrate* added to a solution of urea mixed with potash, forms a white precipitate containing $\text{COH}_2\text{N}_2.2\text{Hg}$. With *mercuric chloride* a white precipitate is formed, which, on heating with water, turns yellow, and is converted into $\text{COH}_2\text{N}_2.3\text{HgO}$. On adding *mercuric oxide* to a warm solution of urea, the compound, $\text{COH}_2\text{N}_2.\text{Hg}$, appears to be produced.

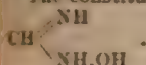
3. With Salts.—On evaporating a solution of urea mixed with *potassium chloride*, the compound $\text{COH}_2\text{N}_2.\text{NaCl}$ is obtained in shining prisms. The compound $\text{COH}_2\text{N}_2.\text{AgNO}_3$, obtained in a similar manner, forms large rhombic prisms.

Isouretine, $\text{CH}_4\text{N}_2\text{O}$, isomeric with urea, is formed by direct condensation of hydrogen cyanide (carbunide) with hydroxylamine $\text{CNH} + \text{NH}_4\text{OH}$.

$\text{CH}_3\text{N}_2\text{O}$, and is obtained by evaporation in long colorless needles, having a strong alkaline reaction, and melting at 104°C . (219.2°F). Its hydrochloride, $\text{CH}_3\text{N}_2\text{O}.\text{HCl}$, forms deliquescent rhombic plates.

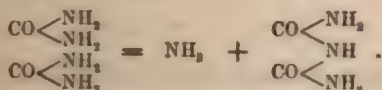
Isuretine decomposes above its melting-point, yielding a sublimate of ammonium carbonate, and a residue containing ammeline (p. 549). Its aqueous solution also decomposes when evaporated, giving off nitrogen, ammonia, and carbon dioxide, and leaving a residue containing urea and biuret.

The constitution of isuretine may perhaps be represented by the formula



Hydroxyl-carbamide or Hydroxyl-urea, $\text{CH}_3\text{N}_2\text{O}_2 = \text{CO} \begin{array}{c} \text{NH.OH} \\ \diagdown \\ \text{NH}_2 \end{array}$, is prepared by adding a strong solution of potassium cyanate to a solution of hydroxylamine nitrate cooled to -10°C . (14°F). It dissolves easily in water and in alcohol, and is precipitated from these solutions by ether in white needles melting at $128^\circ\text{--}130^\circ\text{C}$. ($262.4^\circ\text{--}266^\circ\text{F}$).

Biuret, $\text{C}_2\text{H}_3\text{N}_3\text{O}_2$, is produced by heating urea to $150^\circ\text{--}160^\circ\text{C}$. ($302^\circ\text{--}320^\circ\text{F}$), the change consisting in the separation of one molecule of ammonia from two molecules of urea:

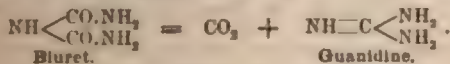


The biuret is extracted from the residue by cold water. It is easily soluble in water and in alcohol, and crystallizes in slender needles containing one molecule of water. Its aqueous solution, mixed with potash, dissolves cupric oxide with red-violet color.

Biuret heated above 170°C . (338°F .) is resolved into ammonia and cyanuric acid:—



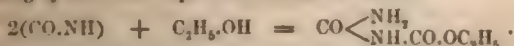
When heated in a stream of gaseous hydrogen chloride, it yields cyanuric acid, urea, and guanidine, CH_3N_3 , together with ammonia and carbon dioxide. The formation of guanidine is represented by the equation:



Ethyl Allophanate, $\text{C}_2\text{H}_3(\text{C}_2\text{H}_5)_2\text{N}_2\text{O}_3 = \text{CO} \begin{array}{c} \text{NH}_2 \\ \diagdown \\ \text{NH.CO.OC}_2\text{H}_5 \end{array}$, or $\begin{array}{c} \text{NH} \begin{array}{c} \text{CO.NH}_2 \\ \diagdown \\ \text{CO.OC}_2\text{H}_5 \end{array} \end{array}$, is produced by the action of ethyl chlorocarbonate on urea:



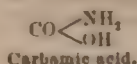
or by passing cyanic acid vapor into absolute alcohol:



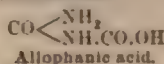
This ether forms shining prismatic crystals, soluble in hot water and in alcohol. Treated with caustic baryta, it yields the barium salt of allophanic acid, $\text{C}_2\text{H}_3\text{N}_2\text{O}_3$, but the acid itself cannot be obtained in the free

state, as, when separated from the barium salt by a mineral acid, it is immediately resolved into urea and carbon dioxide. A series of allophanic ethers may, however, be prepared by the action of cyanic acid on various alcohols.

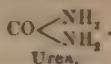
Allophanic acid is related to biuret in the same manner as carbamic acid to urea:



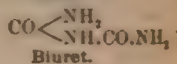
Carbamic acid.



Allophanic acid.



Urea.



Biuret.

In other words, biuret is the amide of allophanic acid.

Trigenic Acid, $\text{C}_4\text{H}_7\text{N}_3\text{O}_2 = \text{CO} \begin{array}{c} \text{NH}_2 \\ \text{NH.CO.N}=\text{C}_2\text{H}_5 \end{array}$, is produced by passing cyanic acid vapor into cold aldehyde:

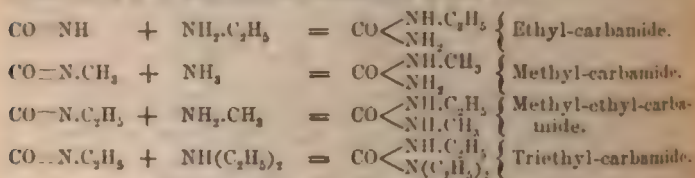


It crystallizes in prisms slightly soluble in water and in alcohol, and decomposing when heated.

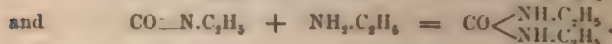
Derivatives of Carbamide.—Compound Ureas.

The hydrogen in carbamide may be replaced by alcoholic or by acid radicles.

1. The alcoholic derivatives are formed by processes similar to those which yield carbamide itself, namely, by the action of amines on cyanic acid, or of ammonia and amines on cyanic ethers:



They are also produced by heating isocyanic ethers with water, the reaction apparently taking place by two stages, thus:



These compounds greatly resemble urea in their properties and reactions. They combine with one equivalent of an acid. By boiling with alkalis they are resolved into carbon dioxide and amines.

Methyl-carbamide, $\text{CO} \begin{array}{c} \text{NH.CH}_3 \\ \text{NH}_2 \end{array}$, crystallizes in long transparent prisms. Its aqueous solution is neutral to test-paper, and if somewhat concentrated yields with nitric acid a precipitate of the salt $\text{C}_2\text{H}_5\text{N}_2\text{O.HNO}_2$.

Dimethyl-carbamide, $\text{CO} \begin{array}{c} \text{NH.CH}_3 \\ \text{NH.CH}_3 \end{array}$, produced by the action of

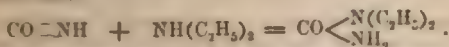
Water or of methylamine on methyl cyanate, crystallizes easily, melts at 70° C. (206.6° F.), volatilizes without alteration, and forms with nitric acid the salt $C_2H_5N_2O.HNO_3$.

Ethyl-carbamide, $CO \begin{smallmatrix} \text{NH.C}_2\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$, forms large prisms, easily soluble in water and in alcohol, melting at 92° C. (197.6° F.). Nitric acid does not precipitate its aqueous solution, but crystals of the nitrate $C_2H_5N_2O.NO_3$ are obtained on evaporation.

Diethyl-carbamide, $CON_2H_5(C_2H_5)_2$.—Of this compound there are two modifications.

• *Diethyl-carbamide*, $CO \begin{smallmatrix} \text{NH.C}_2\text{H}_5 \\ \text{NH.C}_2\text{H}_5 \end{smallmatrix}$, formed by the action of water or of methylamine on ethyl cyanate (see above), crystallizes in long prisms, melts at 112° C. (233.6° F.), and boils without decomposition at 265° C. (505.4° F.).

• *Diethyl-carbamide*, $CO \begin{smallmatrix} \text{N(C}_2\text{H}_5)_2 \\ \text{NH}_2 \end{smallmatrix}$, is formed by the action of diethylamine on cyanic acid :



melts at 97° C. (206.6° F.), and boils at 270°–280° C. (518°–536° F.).

Methyl-ethyl-carbamide, $CO \begin{smallmatrix} \text{NH.CH}_3 \\ \text{NH.C}_2\text{H}_5 \end{smallmatrix}$, formed by the action of methylamine on ethyl isocyanate, is very deliquescent.

Triethyl-carbamide, $CO \begin{smallmatrix} \text{N(C}_2\text{H}_5)_3 \\ \text{NH.C}_2\text{H}_5 \end{smallmatrix}$, is easily soluble in water, alcohol, and ether, melts at 53° C. (127.4° F.), and distils at 223° C. (434° F.).

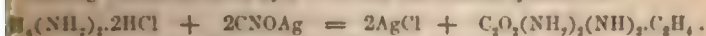
Allyl-carbamide, $CO \begin{smallmatrix} \text{NH.C}_3\text{H}_5 \\ \text{NH}_2 \end{smallmatrix}$, from allyl isocyanate and ammonia, crystallizes in fine prisms.

Diallyl-carbamide or *Sinapoline*, $CO \begin{smallmatrix} \text{NH.C}_3\text{H}_5 \\ \text{NH.C}_3\text{H}_5 \end{smallmatrix}$, is formed by heating allyl isocyanate with water :



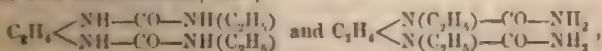
by heating allyl-isothiocyanate, $CS=N.C_3H_5$ (volatile oil of mustard) with water and lead oxide, whereby diallyl-thiocarbamide, $CS(NH.C_3H_5)_2$, is first produced, and then converted into diallyl-carbamide by the action of the lead oxide. Diallyl-carbamide crystallizes in large shining laminae, slightly soluble in water, having an alkaline reaction, and melting at 100°.

Ethene-dicarbamide, $C_2H_{10}N_4O_2 = C_2H_4 \begin{smallmatrix} \text{NH—CO—NH}_2 \\ \text{NH—CO—NH}_2 \end{smallmatrix}$, is formed by heating ethene-diamine hydrochloride with silver cyanate :



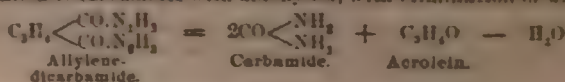
is sparingly soluble in alcohol, easily in hot water, melts with decomposition at 192° C. (377.6° F.).

Diethyl-ethene-carbodiamide, $C_4O_2(NH.C_2H_5)_2(NH)_2(C_2H_4)$, admits of two modifications, viz. :

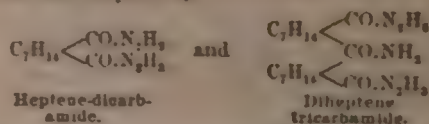


the first produced from ethyl isocyanate and ethene-diamine, the second from cyanic acid and diethyl-ethene-diamine.

Alcoholic carbamides containing diatomic radicles are also produced by combination of carbamides with aldehydes, with elimination of water, *e.g.*



In like manner the compounds,



are produced from carbamide and cenanthol. All these aldehydic carbamides are resolved by boiling with water into carbamide and aldehyde.

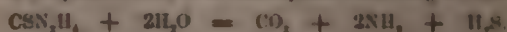
2. **Containing Acid Radicles.**—Carbamides containing monatomic acid radicles are formed by the action of acid chlorides or anhydrides on carbamide. They are not capable of forming salts with acids. Alkalis decompose them into carbamide and the corresponding acid.

Acetyl-carbamide, $\text{CO} \begin{array}{c} \text{NH.C}_2\text{H}_5\text{O} \\ \text{NH}_2 \end{array}$, crystallizes in long, silky needles, melting at 112°C . (233.6°F .), slightly soluble in cold water and alcohol, decomposed by heating into acetamide and cyanuric acid.—*Triacetyl-carbamide*, $\text{C}_6\text{H}_5\text{CIN}_2\text{O}_3 = \text{CO}(\text{NH}_2)(\text{NH.C}_6\text{H}_5\text{CO})$, forms laminae, insoluble in water, and is resolved by heat into hydrochloric acid and hydroantoin, $\text{C}_6\text{H}_5\text{N}_2\text{O}_2$.—*Bromacetyl-carbamide*, $\text{C}_6\text{H}_5\text{BrN}_2\text{O}_3$, crystallizes in needles slightly soluble in water, and is decomposed by heat in a similar manner.

Diacetyl-carbamide, $\text{CO}(\text{NH.C}_2\text{H}_5\text{O})_2$, produced by the action of acetic anhydride on carbamide, or of carbonyl-chloride on acetamide, crystallizes in needles, and sublimes without decomposition.

Carbamides containing diatomic acid-radicles, such as *glycid-carbamide*, $\text{CO} \begin{array}{c} \text{NH} \\ \text{NH} \end{array} \text{C}_2\text{H}_4\text{O}$, are obtained as derivatives of uric acid, and will be described in connection therewith.

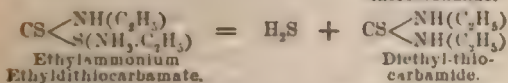
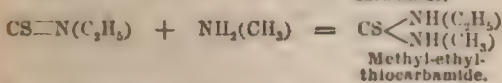
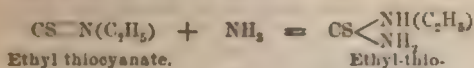
Thiocarbamide or Thio-urea, $\text{CS} \begin{array}{c} \text{NH}_2 \\ \text{NH}_2 \end{array}$, also called *Sulphocarbamide* and *Sulphurea*.—This compound is formed by heating ammonium thiocyanate to 170°C . (338°F .) in the same manner as carbamide is formed from ammonium cyanate. It crystallizes in silky needles or thick rhombic prisms, easily soluble in water and alcohol, sparingly in ether, melts at 146°C . (294.8°F .), and decomposes at a higher temperature, giving off carbon disulphide, hydrogen sulphide, and ammonia, and leaving melon, (p. 549). When heated with water to 140°C . (284°F .) it is reconverted into ammonium sulphocyanate, and by boiling with alkalis, or with hydrochloric or sulphuric acid, it is decomposed according to the equation:



In contact with the oxides of silver, mercury, or lead, and water, it is converted at ordinary temperatures into cyanamide, CN.NH_2 , and by boiling into dicyanodiamide, $\text{C}_2\text{N}_4\text{H}_4$, (p. 448).

Thiocarbamide, like carbamide, forms salts containing one equivalent of acid. The *nitrate*, $\text{CSN}_2\text{H}_4\cdot\text{HNO}_3$, forms large crystals.

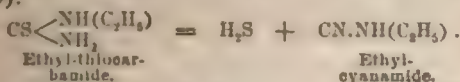
Alcoholic derivatives of thiocarbamide are formed by the processes similar to those employed in the preparation of the alcoholic carbamides ;



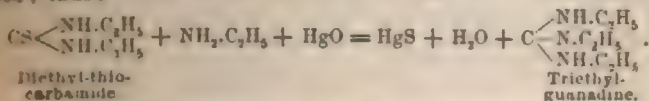
These compounds are desulphurized by heating them with water and mercuric oxide, the sulphur being replaced by oxygen. Those containing two equivalents of alcohol-radicles are converted by this reaction into the corresponding carbamides :



whereas the mono-substituted derivatives are converted, by further separation of hydrogen sulphide, into alcoholic cyanamides (melamines, p. 549):

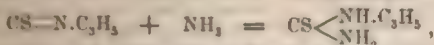


When the bisubstituted thiocarbamides are heated with mercuric oxide and amines, the oxygen of the substituted carbamide formed in the first instance is replaced by imidogen, NH , and substituted guanidines are produced ; thus :



Ethyl-thiocarbamide, $\text{CS}(\text{NH}_2)(\text{NH.C}_2\text{H}_5)$, crystallizes in needles melting at 89°C . (192.2°F .). *Diethyl-thiocarbamide*, $\text{CS}(\text{NH.C}_2\text{H}_5)_2$, forms large crystals sparingly soluble in water, and melting at 77°C . (170.6°F .). *Methyl-ethyl-thiocarbamide*, $\text{CS}(\text{NH.CH}_3)(\text{NH.C}_2\text{H}_5)$, melts at 54°C . (129.2°F .).

Allyl-thiocarbamide, or *Thiosinamine*, $\text{CS} \begin{array}{c} \text{NH.C}_2\text{H}_5 \\ \text{NH}_2 \end{array}$, obtained by combination of allylthiocarbimide (mustard-oil) with ammonia :



crystallizes in shining rhombic prisms, having a bitter taste, melting at 70°C . (158°F .), and decomposing at a higher temperature ; easily soluble in water, alcohol, and ether. Its salts are decomposed by water. By boiling with mercuric oxide or lead oxide and water, it is converted into allyl-cyanamide, $\text{CN.NH.C}_2\text{H}_5$, which is then further converted, as above explained, into triallylmelamine or sinnamine, $\text{C}_3\text{N}_3(\text{NH.C}_2\text{H}_5)_3$.

CARBAMIDES CONTAINING DIATOMIC ACID RADICLES:
URIC ACID AND UREIDEN.

Uric Acid, $C_5N_4H_4O_6$, formerly called *Lithic acid*, is a product of the animal organism, and has never been formed by artificial means. It may be prepared from human urine by concentration and addition of hydrochloric acid, and crystallizes out after some time in the form of small, red-dish, translucent grains, very difficult to purify. A much preferred method is to employ the solid white excrement of serpents, which can be easily procured: this consists almost entirely of uric acid and ammonium urate. It is reduced to powder, and boiled in dilute solution of caustic potash: the liquid, filtered from the insignificant residue of feculent matter and earthy phosphates, is mixed with excess of hydrochloric acid, boiled for a few minutes, and left to cool. The product is collected on a filter, washed until free from potassium chloride, and dried by gentle heat.

Uric acid, thus obtained, forms a glistening, snow-white powder, tasteless, inodorous, and very sparingly soluble. It is seen under the microscope to consist of minute, but regular crystals. It dissolves in concentrated sulphuric acid without apparent decomposition, and is precipitated by dilution with water. By destructive distillation, uric acid yields cyanic acid, hydrocyanic acid, carbon dioxide, ammonium carbonate, and a last, but not only residue, rich in nitrogen. By fusion with potassium hydroxide, it yields potassium carbonate, cyanate, and cyanide. When treated with nitric acid and with lead dioxide, it undergoes decomposition in a manner to be presently described.

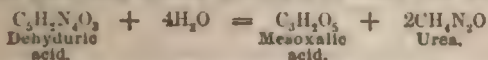
Uric acid is bibasic: its most important salts are those of the alkali metals. *Acid potassium urate*, $C_5N_4H_2K_2O_6$, is deposited from a hot saturated solution of uric acid in the dilute alkali, as a white, sparingly soluble concrete mass, composed of minute needles: it requires about 500 parts of cold water for solution, is rather more soluble at a high temperature, and much more soluble in excess of alkali. *Sodium urate* resembles the potassium salt: it forms the chief constituent of the gouty concretions in the joints, called *chalk-stones*. *Ammonium urate* is also a sparingly soluble compound, requiring for solution about 1000 parts of cold water: the solubility is very much increased by the presence of a small quantity of certain salts, as sodium chloride. The most common of the urinary deposits forming a buff-colored or pinkish cloud or muddiness, which disappears by redissolution when the urine is warmed, consists of a mixture of different urates.

Uric acid is perfectly well characterized, even when in very small quantity, by its behavior with nitric acid. A small portion, mixed with a drop or two of nitric acid in a small porcelain capsule, dissolves with copious effervescence. When this solution is cautiously evaporated nearly to dryness, and, after the addition of a little water, mixed with a slight excess of ammonia, a deep-red tint of murexide is immediately produced.

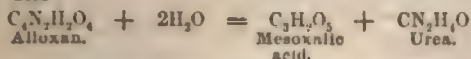
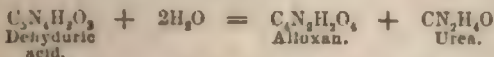
Impure uric acid, in a more or less advanced stage of decomposition as imported into this country, in large quantities, for use as a manure, under the name of *guano* or *hano*. It comes chiefly from the barren and uninhabited islets of the western coast of South America, and is the production of the countless birds that dwell undisturbed in those regions. The people of Peru have used it for ages. Guano usually appears as a pale brown powder, sometimes with whitish specks; it has an extremely offensive odor, the strength of which, however, varies very much. It is soluble in great part with water, and the solution is found to be extremely caustic. Ammonium oxalate, the acid having been generated by a process of oxidation. Guano also contains a base called guanidine.

Products formed from Uric Acid by Oxidation, etc.

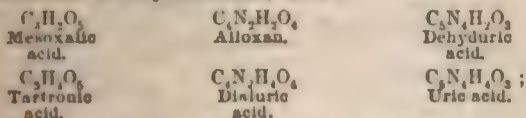
When uric acid is subjected to the action of an oxidizing agent in presence of water, it gives up two of its hydrogen-atoms to the oxidizing agent, while the dehydrogenized residue (which may be called dehydric acid) reacts with water to form mesoxalic acid and urea:



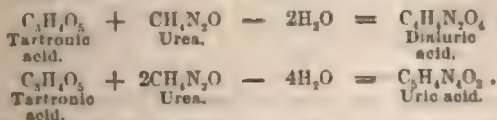
The separation of the urea generally takes place, however, by two stages, the first portion being removed more easily than the second; thus, when dilute nitric acid acts upon uric acid, alloxan is produced; and this, when heated with baryta-water, is further resolved into mesoxalic acid and urea:



Alloxan is a *monureide* of mesoxalic acid—that is to say, it is a compound of that acid with one molecule of urea minus $2\text{H}_2\text{O}$; and the hypothetical dehydric acid is the *diureide* of the same acid, derived from it by addition of 2 molecules of urea and subtraction of 4 molecules of water. Now, by hydrogenizing mesoxalic acid, we obtain tartronic acid, $\text{C}_3\text{H}_4\text{O}_5$ (p. 758); and by hydrogenizing alloxan, we obtain dialuric acid, which two bodies, accordingly, bear to uric acid the same relation that mesoxalic acid and urea bear to dehydric acid; thus:



and just as the hypothetical dehydric acid yields mesoxalic acid and alloxan, so should actual uric acid yield tartronic and dialuric acids. These bodies, however, have not been obtained by the direct breaking-up of uric acid, but only by rehydrogenizing the mesoxalic acid and alloxan which result from the breaking-up of its dehydrogenized product. Provisionally, however, dialuric and uric acids may be regarded as tartronureide and tartron-diureide respectively:



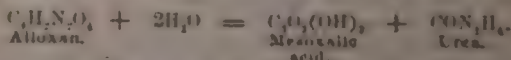
The bodies just mentioned may be regarded as typical of three well-defined classes of compounds, to one or other of which a very large number of uric acid products may be referred, viz.: (1) Non-azotized bibasic acids, such as mesoxalic and tartronic acid; (2) Monureides, such as dialuric acid and alloxan, containing a residue or radicle of such an acid, e. g., mesoxalyl, C_3H_3 , plus one urea-residue, $\text{CO} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}$; (3) Diureides, such as uric acid itself, containing an acid residue, together with two urea-residues.

Monobridides.

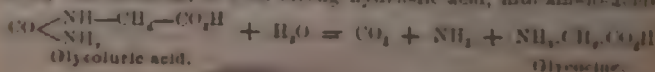
These monobridides may be regarded as carbamides or ureas, in which part of the nitrogen (forming a chain) is replaced by diatomic substituents. They are either diatomic compounds belonging to the monobridide series, and containing the radical $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \\ \diagdown \end{smallmatrix} \text{CO}$ (usually CO_2), or radicals derived from one or diatomic compounds belonging to the oxide series, and containing the radical $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \\ \diagdown \end{smallmatrix} \text{CO}$, or others derived therefrom. These relations are exhibited in the following table.

| | |
|--|---|
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \\ \diagdown \end{smallmatrix} \text{CO}$ Urea. | |
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{COOH} \\ \diagdown \end{smallmatrix} \text{COOH}$ Monocarbolic acid. | $\text{CO} \begin{smallmatrix} \diagup \\ \text{COOH} \\ \diagdown \end{smallmatrix} \text{COOH}$ Oxalic acid. |
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{CO}$ Ketoxycarbonylurea
Alloxan. | $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{CO}$ Oxalylurea
Parabarbitalic acid. |
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{CH}_2\text{OH}$ Tetroxycarbonylurea
Isobarbitalic acid. | $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{CH}_2\text{OH}$ Oxalylglyoxylylurea
Allobarbitalic acid. |
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{CH}_3$ Monoxycarbonylurea
Barbitalic acid. | $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{H}$ Glyoxylurea
Hydrobarbitalic acid. |
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \text{---} \text{CO} \text{---} \text{CO}_2\text{H} \\ \diagdown \end{smallmatrix}$ Alloxanic acid. | $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \text{---} \text{CO}_2\text{H} \\ \diagdown \end{smallmatrix}$ Oxaloxalic acid. |
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{CH}_2\text{NH}_2$ Amidobarbitalic acid
Uranil. | $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \text{---} \text{CO}_2\text{NH}_2 \\ \diagdown \end{smallmatrix}$ Oxalureamide. |
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{CH}_2\text{NO}_2$ Nitrobarbitalic acid
Isobarbitalic acid. | $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CH}_2 \text{---} \text{CO}_2\text{H} \\ \diagdown \end{smallmatrix}$ Glyoxylurea
Glycolytic acid. |
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{CH}_2\text{NO}$ Nitrobarbitalic acid. | |
| $\text{CO} \begin{smallmatrix} \diagup \\ \text{NH} \text{---} \text{CO} \\ \diagdown \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \\ \text{NH}_2 \\ \diagdown \end{smallmatrix} \text{SO}_3\text{OH}$ Thionuric acid. | |

Most of these compounds, when treated with alkalis, are resolved into the corresponding diatomic acids and urea, or the products of decomposition. e. g.,



Those which contain the group NH_2 united with CH_2 , are converted on boiling with alkalis, or with strong hydrosulphic acid, into amides, acids.



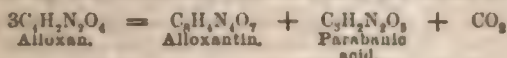
1. Mesoxalic Series.

Alloxan, $C_4H_2N_2O_4$.—This is the characteristic product of the action of strong nitric acid on uric acid in the cold. It is best prepared by adding 1 part of pulverized uric acid to 3 parts of nitric acid, specific gravity 1.45, in a shallow basin standing in cold water. The resulting white crystalline mass, after standing for some hours, is drained from the acid liquid in a funnel having its neck stopped with pounded glass, then dried on a porous tile, and purified by crystallization from a small quantity of water.

Alloxan crystallizes by slow cooling from a hot saturated solution in large efflorescent rectangular prisms containing $C_4H_2N_2O_4 + 4Aq.$; from a solution evaporated by heat it separates in monoclinic octohedrons with truncated summits, containing $C_4H_2N_2O_4 + Aq.$ These crystals heated to 150°C – 160°C . (302°C – 320°F .) in a stream of hydrogen give off their water, and leave anhydrous alloxan, $C_4H_2N_2O_4$. Alloxan is very soluble in water: the solution has an acid reaction, a disagreeably astringent taste, and stains the skin, after a time, red or purple. It forms a deep-blue compound with a ferrous salt and an alkali, and its solution, mixed with hydrocyanic acid and ammonia, yields a white precipitate of oxaluramide; these two reactions are very characteristic.

Alloxan unites (like ketones) with alkaline bisulphites, forming crystalline compounds.

Its aqueous solution decomposes gradually at ordinary temperatures, more quickly on boiling, into alloxantin, parabanic acid, and carbon dioxide:

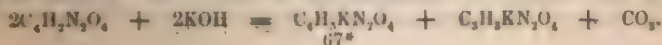


By boiling with dilute acids, alloxan is resolved into oxalic acid and urea; by boiling with baryta-water or lead acetate, it is first converted into alloxanic acid, which then splits up into urea and mesoxalic acid. By hydriodic acid and other reducing agents, alloxan is converted, especially in the cold, into alloxantin; at higher temperatures into dialuric acid.

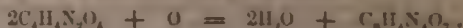
Alloxanic Acid, $C_4H_2N_2O_5$.—The barium-salt of this acid is deposited in small, colorless, pearly crystals, when baryta-water is added to a solution of alloxan heated to 60°C . (140°F .), as long as the precipitate first produced redissolves, and the filtered solution is then left to cool. The barium may be separated by the cautious addition of dilute sulphuric acid, and the filtered liquid, on gentle evaporation, yields alloxanic acid in small radiated needles. It has an acid taste and reaction, decomposes carbonates, and dissolves zinc with disengagement of hydrogen. It is a bibasic acid. The alloxanates of the alkali-metals are freely soluble: those of the earth-metals dissolve in a large quantity of tepid water; that of silver is quite insoluble and anhydrous.

On boiling its salts with water, the alloxanic acid is resolved into urea and mesoxalic acid. The free acid when boiled yields oxalantin.

Dialuric Acid, $C_4H_2N_2O_6$, is the final product of the action of reducing agents on alloxan, and is formed when sulphuretted hydrogen is passed through a boiling solution of alloxan till no further action takes place: $C_4H_2N_2O_4 + H_2S = C_4H_2N_2O_6 + S$. On adding to an aqueous solution of alloxan, first a small quantity of hydrocyanic acid and then potassium carbonate, the potassium salt of dialuric acid separates out in granular crystals, whilst oxalurate remains dissolved;



Dialuric acid separated from its salts by hydrochloric acid crystallizes in needles, has a strong acid reaction, and when exposed to the air turns red, absorbs oxygen, and is converted into alloxantin:

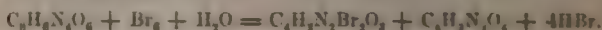


Barbituric Acid, $C_4H_4N_2O_3$, is formed by the action of sodium amalgam or hydriodic acid on dibromobarbituric acid; also by heating a solution of alloxantin with strong sulphuric acid, barbituric acid then separating out, while parabanic acid remains in solution.

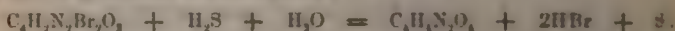
Barbituric acid crystallizes in beautiful prisms, containing two molecules of water. It is bibasic, and yields chiefly acid salts, which are obtained by treating the corresponding acetates with barbituric acid.

Barbituric acid is converted by fuming nitric acid into dilituric acid by potassium nitrate into potassium violurate. When boiled with potash it gives off ammonia, and yields the potassium-salt of malonic acid, $C_3H_4O_4$ (p. 746), whence it appears to have the constitution of malonyl-urea, $CO < \begin{smallmatrix} NH-CO \\ NH-CO \end{smallmatrix} > CH_2$.

Dibromobarbituric acid, $C_4H_2Br_2N_2O_3 = CO < \begin{smallmatrix} NH.CO \\ NH.CO \end{smallmatrix} > CBr_2$, is formed by the action of bromine on barbituric, or on nitro-nitroso-, or amido-barbituric acid; also, together with alloxan, by the action of bromine on hydruilic acid:



It crystallizes in colorless, shining plates, or prisms, soluble in water, very soluble in alcohol and ether. By hydrogen sulphide, in presence of water, it is reduced to dialuric acid:



When chlorine or bromine acts upon a warm solution of dibromobarbituric acid, carbon dioxide is eliminated and tribromomethyluric acid

$CO < \begin{smallmatrix} NH.CO.CBr_2 \\ NH_2 \end{smallmatrix} >$, is produced. This compound melts at $145^\circ C.$ ($293.4^\circ F.$), and yields bromoform when boiled with water.

Monobromobarbituric acid, $C_4H_3BrN_2O_3$, produced by the action of zinc or aqueous hydrocyanic acid on dibromobarbituric acid, forms crystals sparingly soluble in water.

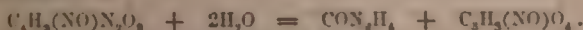
Nitrobarbituric or Dilituric acid, $C_4H_3(NO_2)N_2O_3$, is formed by the action of fuming nitric acid on barbituric acid, or of ordinary nitric acid on hydruilic acid. It crystallizes in colorless square prisms containing $3H_2O$, soluble in water with yellow color. It appears to be tribasic, but is most inclined to form salts containing only one equivalent of metal. Its salts are very stable, most of them resisting the action of mineral acids. By heating with bromine, it is converted into dibromobarbituric acid.

Nitrosobarbituric or Violuric acid, $C_4H_3(NO)N_2O_3$, is formed by the action of nitric acid of specific gravity 1.2 on hydruilic acid, also by that of potassium nitrite on barbituric acid. The resulting solution is mixed with barium chloride, and the barium salt thereby precipitated is decomposed by sulphuric acid.

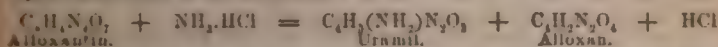
Violuric acid crystallizes in yellow rhombic octohedrons containing one molecule of H_2O , moderately soluble in water. It forms blue, violet, or yellow salts containing one equivalent of metal. The potassium salt, $C_4H_2K(NO)N_2O_3 + 2H_2O$, forms dark blue prisms, dissolving in water with

violet color. The sodium salt is dark red. The solution of the acid is colored dark blue by ferric acetate, and on adding alcohol to the solution, a ferric salt is precipitated in six-sided laminae having a red color and metallic lustre.

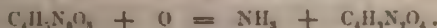
Violuric acid heated with potash-lye is resolved into urea and nitrosomalonic acid :



Amidoharbituric acid, $C_4H_3(NH_2)N_2O_3$, also called *Uramil*, *Dialuramide*, and *Mucosan*, is formed by the action of hydriodic acid on violuric acid or diluric acid, or by boiling a solution of ammonium thionurate with hydrochloric acid. It is best prepared by boiling alloxantin with an aqueous solution of sal-ammoniac :

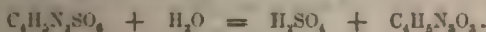


It crystallizes in colorless needles, turning red on exposure to the air, nearly insoluble in cold water, slightly soluble in boiling water, easily in alkalis. The ammoniacal solution becomes purple on exposure to the air, and yields murexid on boiling. Uramil is decomposed by strong nitric acid, with formation of ammonium nitrate and alloxan :



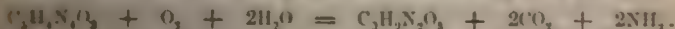
Heated with aqueous potassium cyanate it is converted into pseudouric acid (p. 802): $C_4H_3N_3O_3 + CNHO = C_4H_3N_4O_4$.—By the action of mercuric or argentic oxide suspended in boiling water, it is converted into murexid.

Thionuric Acid, $C_4H_3N_2SO_3 = CO \begin{smallmatrix} \text{NH} - \text{CO} \\ \text{NH} - \text{CO} \end{smallmatrix} C \begin{smallmatrix} \text{NH}_2 \\ \text{SO}_3\text{H} \end{smallmatrix}$.—This acid, which contains the elements of alloxan, ammonia, and sulphurous oxide ($C_4H_3N_2O_4 + NH_3 + SO_2$), is formed, as an ammonium-salt, when a cold solution of alloxan is mixed with a saturated aqueous solution of sulphurous acid, in such quantity that the odor of the gas remains quite distinct: an excess of ammonium carbonate mixed with a little caustic ammonia is then added, and the whole boiled for a few minutes. On cooling, ammonium thionurate is deposited in colorless, crystalline plates, which, by solution in water and recrystallization, acquire a fine pink tint. By converting it into a lead salt, and decomposing the latter with hydrogen sulphide, thionuric acid is obtained as a white crystalline mass, very soluble in water. When its solution is heated to the boiling point, it is resolved into sulphuric acid and uramil :



2. Oxalic Series.

Parabanic Acid, $C_3H_2N_2O_5 = CO \begin{smallmatrix} \text{NH} - \text{CO} \\ \text{NH} - \text{CO} \end{smallmatrix}$, *Oxalyl urea*.—This is the characteristic product of the action of moderately strong nitric acid on uric acid or alloxan, with the aid of heat; formed also from the same substances by oxidation with manganese dioxide and sulphuric acid :



It is conveniently prepared by heating 1 part of uric acid with 8 parts of nitric acid till the reaction has nearly ceased; the liquid is evaporated to

a syrup and left to cool; and the product drained from the mother-liquor is purified by re-crystallization. Parabanic acid forms colorless, transparent, thin, prismatic crystals, permanent in the air: it is easily soluble in water, has a pure and powerfully acid taste, and reddens litmus strongly. Neutralized with ammonia, and boiled for a moment, it yields on cooling crystals of the ammonium salt of oxaluric acid, $C_3H_4N_4O_6$, from which the acid may be separated by sulphuric acid.

Parabanic acid is bibasic. With the alkali-metals it forms monometallic salts, like $C_3HKN_2O_5 = CO \begin{smallmatrix} \text{NK} - \text{CO} \\ \text{NH} - \text{CO} \end{smallmatrix}$, which are obtained as crystalline

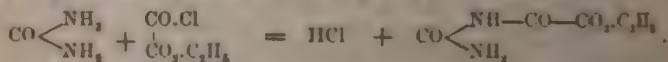
precipitates on adding potassium- or sodium-ethylate to a solution of parabanic acid in absolute alcohol; when dissolved in water, these salts are converted into oxalates. Silver nitrate, added to a solution of the acid, throws down the diargentate salt, $C_3Ag_2N_2O_5$.

Parabanic acid boiled with dilute acids is resolved into urea and oxaluric acid. In presence of alkalis, it takes up water, and is converted into oxaluric acid, $C_3H_4N_4O_6$. By the action of zinc and hydrochloric acid, it is converted into oxalantin, $C_6H_8N_4O_8 = 2C_3H_4N_2O_5 - O$.

Methyl-parabanic acid, $C_3H(CH_3)N_2O_5$, is obtained by decomposition of creatinine.

Dimethyl-parabanic acid or *Cholestrophane*, $C_3(CH_3)_2N_2O_5$, obtained by heating the silver salt of parabanic acid with methyl iodide, forms silvery laminae, which easily melt and sublime.

Oxaluric Acid, $C_3H_4N_4O_6 = CO \begin{smallmatrix} \text{NH} - \text{CO} - \text{CO}_2H \\ \text{NH}_2 \end{smallmatrix}$, the analogue of alloxanic acid, is formed by the action of alkalis on parabanic acid. Its ethylic ether is produced by heating urea with chloroacetic ether:



It crystallizes in silky needles, which melt with decomposition at $150 - 160^\circ \text{C}$. ($302^\circ - 320^\circ \text{F}$).

Oxaluric acid, separated from its salts by a mineral acid, is a heavy crystalline powder. Its salts are sparingly soluble. Boiled with water or alkalis, it is resolved into oxalic acid and urea. Heated to 200°C . (392°F .) with phosphorus trichloride, it gives up water, and is converted into parabanic acid.

Oxaluramide or **Oxalan**, $C_3H_3N_3O_5 = CO \begin{smallmatrix} \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$, is formed, together with dialuric acid, on adding a little hydrocyanic acid and ammonia to an aqueous solution of alloxan, and separated as a white precipitate, while the dialuric acid remains dissolved. It is also produced by heating ammonium parabamate (its isomeride) to 100°C , and by heating ethyloxalurate with ammonia. It is sparingly soluble in water, and is resolved by boiling with water, into oxalic acid, urea, and ammonia.

Allanturic Acid or **Oxyglycolyl-urea**, $C_3H_4N_4O_5 = CO \begin{smallmatrix} \text{NH} - \text{CH}(\text{OH}) \\ \text{NH} - \text{CO} \end{smallmatrix}$, formed by heating allantoin with baryta-water or dioxide of lead, is a deliquescent mass, the aqueous solution of which gives white precipitates with silver or lead salts. When boiled with baryta, it yields hydantoic and parabanic acids, the latter further splitting up into oxaluric acid and urea (or CO_2 and NH_3).

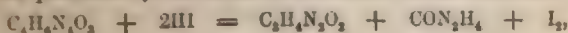
Succinuric Acid, $C_3H_5N_2O_4$, is produced by heating urea to 120° – 130° C. (248 – 266° F.) with succinic anhydride. It forms shining scales, melting with decomposition at 203° – 205° C. (397.4° – 401° F.).

Hydantoin or Glycolyl-urea, $C_3H_4N_2O_3 = CO \begin{smallmatrix} \text{NH} - \text{CO} \\ | \\ \text{NH} - \text{CH}_2 \end{smallmatrix}$,

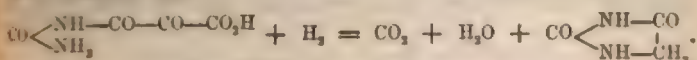
is formed synthetically by heating bromacetyl-urea, with alcoholic ammonia:



It is also produced by the action of hydriodic acid on allantoin:

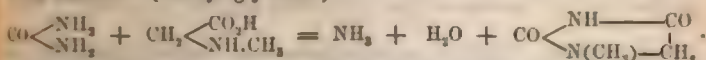


or on alloxanic acid:



Hydantoin forms needle-shaped crystals, having a faint sweet taste, and melting at 206° C. (402.8° F.). When boiled with baryta-water, it takes up water and is converted into hydantoic acid.

Methyl-hydantoin, $CO \begin{smallmatrix} \text{NH} - \text{CO} \\ | \\ \text{N}(\text{CH}_3) - \text{CH}_2 \end{smallmatrix}$, is obtained by prolonged heating of creatinine (*q. v.*) to 100° with baryta-water; also by fusing urea with sarcosine (methyl-glycocine):



It forms crystals easily soluble in water and in alcohol, melts at 145° C. (293° F.), and sublimes in shining needles. Boiled with oxide of mercury or silver it yields metallic derivatives.

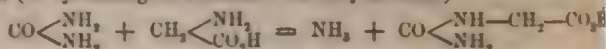
Lactyl-urea, $CO \begin{smallmatrix} \text{NH} - \text{CO} \\ | \\ \text{NH} - \text{CH} - \text{CH}_3 \end{smallmatrix}$, metameric with methyl-hydantoin, is formed, together with alanine, when the potassium cyanide used in the preparation of the latter from aldehyde-ammonia (p. 792) contains cyanate. It forms efflorescent rhombic crystals, containing $C_3H_6N_2O_3 + \text{H}_2\text{O}$; melts at 140° C. (284° F.), and sublimes with partial decomposition. By boiling with baryta-water it is converted into lacturic acid,

$CO \begin{smallmatrix} \text{NH} - \text{CH} - \text{CH}_3 \\ | \\ \text{NH}_2 - \text{CO}_2\text{H} \end{smallmatrix}$, metameric with methyl-hydantoic acid, which melts at 155° C. (311° F.).

Ethyl-hydantoin, $CO \begin{smallmatrix} \text{NH} - \text{CO} \\ | \\ \text{N}(\text{C}_2\text{H}_5) - \text{CH}_2 \end{smallmatrix}$, produced in like manner by melting urea with ethyl-glycocine, crystallizes in large, flat prisms, easily soluble in water and alcohol, melting at about 100° , and easily subliming.

The metameric compound, **acetonyl-urea**, $CO \begin{smallmatrix} \text{NH} - \text{C}(\text{CH}_3)_2 \\ | \\ \text{NH} - \text{CO} \end{smallmatrix}$, formed by heating a mixture of acetone and potassium cyanide containing cyanate with fuming hydrochloric acid, crystallizes in prisms, melting at 175° C. (347° F.). By boiling with baryta-water it is converted into acetonuric acid, $C_3H_6N_2O_3$.

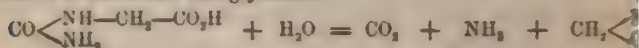
Hydantoic or Glycoluric Acid, $C_3H_4N_2O_3$, = $CO \begin{smallmatrix} \text{NH} \\ \text{NH}_2 \end{smallmatrix} \text{CH}_2 \text{CO}_2H$, is produced by boiling allantoin, hydantoin, glycoluril with baryta-water, and synthetically by heating glycocyl urea (or by boiling its solution with baryta-water):



also by heating glycocine sulphate with potassium cyanate:



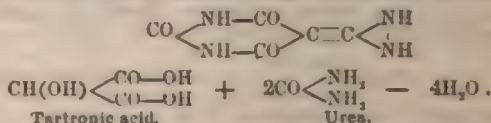
Hydantoic acid forms large rhombic prisms soluble in water. It is basic, and most of its salts are easily soluble. By heating with hydantoin it is converted into glycocine:



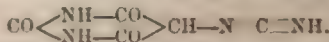
Diureides.

The best known compounds of this class contain 4, 5, 6, or 8 carbon. The 4- and 5-carbon diureides (including uric acid) are formed by the union of one molecule of a bibasic acid and 2 molecules of urea, with elimination of 4 molecules of water, and accordingly contain one diatomic acid-residue and two urea-residues, $CO \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}$.

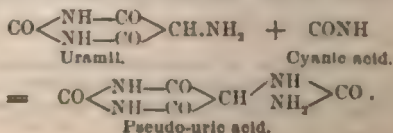
Uric Acid, $C_5H_4N_4O_3$, as already observed, may be regarded as a diureide of tartaric acid, and accordingly represented by the formula:



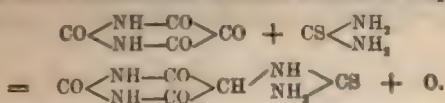
Iso-uric Acid, $C_5H_4N_4O_3$, is formed by the action of cyanogen on alloxantin in aqueous solution, and separates on boiling in the form of a heavy powder. Its constitution may perhaps be represented by the formula:



Pseudo-uric Acid, $C_6H_6N_4O_4$.—The potassium salt of this acid is obtained as a yellow crystalline powder by boiling uramil with a solution of potassium cyanate. The free acid forms colorless crystals slightly soluble in water. Its structure and formation may be represented as follows:



Pseudo-thionric Acid, $C_5H_8N_4O_3S$, is formed by heating alloxan and thiocarbamide with a concentrated alcoholic solution of sulphur dioxide:



It forms thin white needles, insoluble in water, but soluble in acids.

Uroxanic Acid, $C_5H_8N_4O_6$, and **Oxonc Acid**, $C_4H_5N_3O_4$.—These acids are formed by gradual oxidation of uric acid in alkaline solution. A solution of uric acid in potash left for some time in an open vessel deposits shining laminae of potassium uroxanate, $C_5H_8K_2N_4O_6 + 3H_2O$, from which the free acid may be separated by hydrochloric acid in the form of a crystalline powder, which dissolves in hot water, but decomposes at the same time, with separation of carbon dioxide. Its formation is represented by the equation:



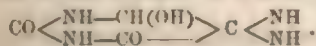
Potassium uroxanate, at the moment of its formation, is partly converted, by separation of CO_2 and NH_3 , into potassium oxonate, $C_4H_5K_2N_3O_4$, which is also formed by passing a stream of air through a solution of uric acid in potash till all the uric acid is oxidized. This salt forms radiate groups of crystals, containing $1\frac{1}{2}$ mol. H_2O . Acetic acid added to its dilute solution throws down the potassium salt of allanturic acid, or oxygly-

colyl-urea, $C_5H_8N_4O_5$, or $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CHOH} \\ \text{NH} \text{---} \text{CO} \end{array}$.

Allantoin, $C_4H_6N_4O_3$.—This substance, which contains the elements of 2 molecules of ammonium oxalate minus 5 molecules of water [$2C_2(NH_4)_2O_4 - 5H_2O$], is found in the allantoinic liquid of the foetal calf and in the urine of the sucking calf. It is produced artificially, together with oxalic acid and urea, by boiling uric acid with lead dioxide and water: $C_5H_8N_4O_3 + O_2 + 5H_2O = C_4H_6N_4O_3 + 2C_2H_2O_4 + 2CH_4N_2O_3$.

The liquid filtered from lead oxalate, and concentrated by evaporation, deposits, on cooling, crystals of allantoin, which are purified by re-solution and the use of animal charcoal. The mother-liquor, when further concentrated, yields crystals of pure urea. Allantoin forms small but brilliant prismatic crystals, transparent, colorless, tasteless, and without action on vegetable colors. It dissolves in 160 parts of cold water, and in a smaller quantity at the boiling heat. It is decomposed by boiling with nitric acid, and by oil of vitriol when concentrated and hot, into ammonia, carbon dioxide, and carbon monoxide. Heated with concentrated solutions of caustic alkalies, it is decomposed into ammonia and oxalic acid.

Its structure may, perhaps, be represented by the formula

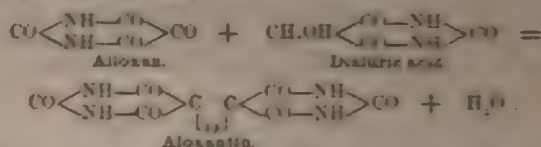


Glycoluril, $C_4H_6N_4O_2$, probably $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CH}_2 \\ \text{NH} \text{---} \text{CO} \end{array} \text{C} \begin{array}{c} \text{NH} \\ \text{NH} \end{array}$, is formed by the action of sodium amalgam on allantoin, and separates in octohedral crystals, sparingly soluble in water, moderately soluble in ammonia and in concentrated acids. Ammoniacal silver nitrate forms in its

gives a yellow precipitate having the composition $C_4H_4N_2O_6$. On boiling with baryta-water it is converted into urea and hydric acid, and on boiling with acids it is converted into hydric acid.

Ureides containing 6 and 8 atoms of carbon are formed by the union of 2 monocarboic molecules, with elimination of water.

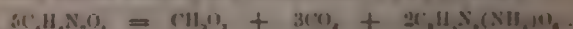
Alloxantin, $C_8H_8N_4O_8$, is formed on mixing the aqueous solution of alloxan and diarsinic acid:



It is the chief product of the action of hot dilute nitric acid upon urea, and is likewise produced by the action of deoxidising agents upon alloxan—anhydrous alloxantin, in fact, containing 1 atom of oxygen less than 2 molecules of alloxan. It is best prepared by passing sulphurous hydrogen gas through a moderately strong and cold solution of alloxan. The mother-liquor from which the crystals of alloxan have separated answers the purpose perfectly well; it is diluted with a little water, and a copious stream of gas transmitted through it. Sulphur is then deposited in large quantity, mixed with a white, crystalline substance, which is the alloxantin. The product is drained upon a filter, slightly washed, and then boiled in water; the filtered solution deposits the alloxantin on cooling. Alloxantin forms small, four-sided, oblique rhombic prisms, colorless and transparent; it dissolves with difficulty in cold water, but more freely at the boiling heat. The solution reddens litmus, gives with baryta-water a violet-colored precipitate, which disappears on heating, and when mixed with silver nitrate produces a black precipitate of metallic silver. Heated with chlorine or nitric acid, it is oxidized to alloxan. The crystals become red when exposed to ammoniacal vapors. They contain 5 mol. H_2O , which they do not give off till heated above $150^\circ C.$ ($302^\circ F.$).

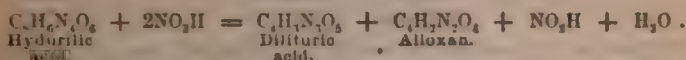
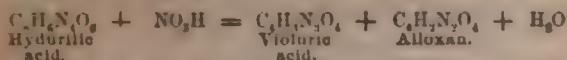
Alloxantin is readily decomposed: when a stream of sulphuretted hydrogen is passed through its boiling solution, sulphur is deposited and diarsinic acid is produced. A hot saturated solution of alloxantin mixed with a neutral salt of ammonia instantly assumes a purple color, which, however, quickly vanishes, the liquid becoming turbid from formation of uramil: the solution then contains alloxan and free acid. With carbon oxide, alloxantin gives off carbon dioxide, reduces a portion of the metal, and converts the remainder of the oxide into oxalurate. Boiled with water and lead dioxide, it gives off urea and lead carbonate.

Hydric Acid, $C_4H_4N_2O_6$.—Diarsinic acid, heated to about $100^\circ C.$ ($212^\circ F.$) with glycerin (which acts merely as a solvent), splits up into formic acid, carbon dioxide, and ammonium hydricate:—



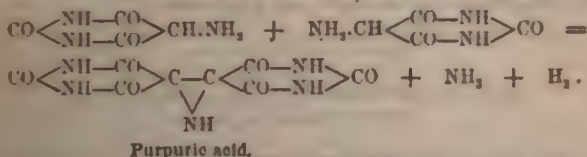
By converting this ammonium salt into a copper salt, and decomposing the latter with H_2S , hydric acid is obtained in crystals.

Hydruillic acid is converted by fuming nitric acid into alloxan, without any other product; but with nitric acid of ordinary strength it yields alloxan, together with violuric acid, violantin, and dilituric acid:

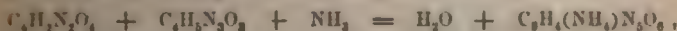


If the action be carried on to the end, dilituric acid is the only product. This acid may indeed be regarded as a product of the oxidation of violuric acid: $\text{C}_4\text{H}_4\text{N}_4\text{O}_6 = \text{C}_4\text{H}_2\text{N}_2\text{O}_4 + \text{O}$: and violantin as a compound of the two.

Purpuric Acid, $\text{C}_6\text{H}_4\text{N}_4\text{O}_6$, is not known in the free state: its ammonium salt, $\text{C}_6\text{H}_4(\text{NH}_4)_2\text{N}_4\text{O}_6$, constitutes murexid. This salt contains the elements of two molecules of uramil minus two atoms of hydrogen:



It is formed by mixing the ammoniacal solutions of alloxan and uramil:



and is best prepared by boiling for a few minutes a mixture of 1 part of dry uramil, 1 part of mercuric oxide, and 40 parts of water rendered slightly alkaline by ammonia:



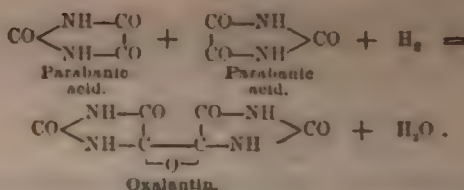
Another method is that of Dr. Gregory: 7 parts of alloxan and 4 parts of alloxantin are dissolved in 240 parts of boiling water, and the solution is added to about 80 parts of cold strong solution of ammonium carbonate: the liquid instantly acquires such a depth of color as to become opaque, and gives on cooling a large quantity of murexid: the operation succeeds best on a small scale.

Murexid* crystallizes with 1 molecule H_2O in small square plates or prisms, which by reflected light exhibit a splendid green metallic lustre, like that of the wing-cases of the rose-beetle and other insects: by transmitted light they are deep purple-red. It dissolves with difficulty in cold water, much more easily at the boiling heat, but is insoluble in alcohol and ether. Mineral acids decompose it, with separation of a white or yellowish substance called murexan, probably identical with uramil. Caustic potash dissolves it, with production of a magnificent purple color, which disappears on boiling.

A few years ago murexid was extensively used in dyeing; but it is now to a great extent superseded by rosaniline.

Oxalantin, $\text{C}_4\text{H}_4\text{N}_4\text{O}_6$, also called *leucoturic acid*, is formed by the action of zinc and hydrochloric acid on parabanic acid:

* So called from the Tyrian dye, said to have been prepared from a species of murex.



It forms small crystals slightly soluble in water, and reduces ammoniacal solutions of mercury and silver.

Allitric Acid, $\text{C}_6\text{H}_8\text{N}_4\text{O}_4$, is formed, together with alloxan and parabanic acid, by boiling alloxantin with hydrochloric acid. It forms crystals sparingly soluble in water, and when heated with water to $180^\circ\text{--}190^\circ\text{C}$. ($356^\circ\text{--}374^\circ\text{F}$.), is resolved into oxalic acid, carbon dioxide and ammonia.

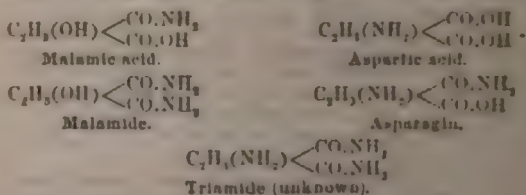
Respecting basic compounds, natural and artificial, related to the ureoles by their composition and reactions, see ALKALOIDS.

AMIDES DERIVED FROM TRIATOMIC AND TETRATOMIC ACIDS.

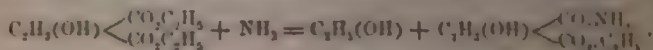
Our knowledge of these amides is somewhat limited: we shall name only those derived from malic, tartaric, and citric acids:

1. Amides of Malic Acid.

Malic acid, $\text{CO}_2\text{H}-\text{CH}_2-\text{CHOH}-\text{CO}_2\text{H}$, or $\text{C}_4\text{H}_5(\text{OH})\begin{array}{c} \text{CO}_2\text{H} \\ | \\ \text{CO}_2\text{H} \end{array}$, which is triatomic and bibasic, is capable of yielding five amides, viz.:

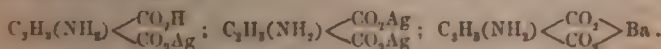


Malamic acid is not known in the free state, but its ethyllic ether, or *Malamethane*, $\text{C}_4\text{H}_5(\text{OH})\begin{array}{c} \text{CO.NH}_2 \\ | \\ \text{CO.C}_2\text{H}_5 \end{array}$, is formed as a crystalline mass when ammonia gas is passed into an alcoholic solution of diethyllic malate.



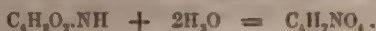
Aspartic acid, $\text{C}_4\text{H}_7\text{NO}_4$, isomeric with malamic acid, is related to malic and succinic acids in the same manner as glycocoll to glycolic and acetic acids (p. 778), and may accordingly be regarded as an amino succinic acid. It occurs in beet-molasses, and is produced by various reactions from albuminous substances. It is prepared by boiling asparagin with alkalis or acids. It crystallizes in small rhombic prisms, moderately soluble in hot water. Its alkaline solutions turn the plane of polarization

to the left: acid solutions to the right. Like other amido-acids, it unites both with acids and with alkalis; with the latter it forms both acid and neutral salts; e. g.,



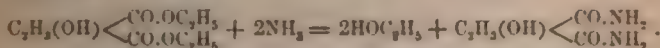
By the action of nitrous acid it is converted into malic acid.

An inactive aspartic acid is obtained by heating fumarimide with water:



It crystallizes in large monoclinic prisms, somewhat more soluble in water than the optically active acid. By nitrous acid it is converted into inactive malic acid.

Malamide, $C_4H_7N_2O_3$, is produced by the action of ammonia in excess on dry diethylic malate:



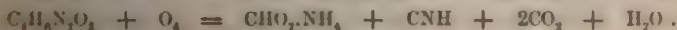
It forms large crystals, and when heated with water is resolved into ammonia and malic acid.

Asparagin, $C_4H_7(NH_2) \begin{matrix} \text{CO.NH}_2 \\ \text{CO.OH} \end{matrix}$, isomeric with malamide, occurs in numerous plants, as asparagus, marsh mallow, mangold-wurzel, peas, beans, vetches, and cereal grasses, especially in the young sprouts. It may be prepared from marsh-mallow roots by chopping them small, macerating them in the cold with milk of lime, precipitating the filtered liquid with barium carbonate, and evaporating the clear solution over the water-bath to a syrup. The asparagin then crystallizes on cooling in shining transparent rhombic prisms, which have a faint cooling taste, and are moderately soluble in hot water, insoluble in alcohol and in ether. The crystals contain one molecule of water, whereas those of malamides are anhydrous.

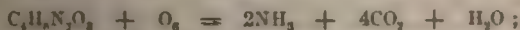
Asparagin and malamide differ also in their action on polarized light, malamide having a specific rotatory power of -47.5° , whereas that of asparagin in an acid solution is $+35^\circ$, and in an ammoniacal solution -11° . Lastly, malamide, when treated with alkalis, is resolved, as already observed, into ammonia and malic acid, whereas asparagin yields ammonia and aspartic acid.

Asparagin forms salts both with acids and with bases.

By fermentation in contact with albuminous substances, asparagin is converted into ammonium succinate. By oxidation with potassium permanganate it yields ammonium formate, hydrocyanic acid, and carbon dioxide:



In presence of sulphuric acid the oxidation takes place according to the equation:



in presence of potash the products are ammonia and oxalic acid:



2. Amides of Tartaric Acid. — *Tartramic Acid*, $C_4H_7NO_3 = C_4H_7(OH)_2 \begin{matrix} \text{CO.NH}_2 \\ \text{CO.OH} \end{matrix}$, is obtained as an ammonium-salt by the action of ammonia on tartaric anhydride, $C_4H_4O_5$.

Ethyl tartrate, *Tartramic ether*, or *Tartramethane*, is obtained by the action of alcoholic ammonia on diethyl tartrate. When cautiously heated with alkalis, it yields tartramic acid. Ammonia converts it into tartramide.

Tartramide, $C_4H_6N_2O_4 = C_2H_2(OH)_2 \begin{smallmatrix} \text{CO.NH}_2 \\ \text{CO.NH}_2 \end{smallmatrix}$, formed also by the action of ammonia on diethyl tartrate, is a crystalline substance, the solution of which exhibits dextro- or levo-rotation according to the kind of tartaric acid from which it has been prepared.

3. **Citramide**, $C_6H_{11}N_3O_4 = C_2H_4(OH)(CO.NH_2)_2$, obtained by the action of alcoholic ammonia on ethyl or methyl citrate, is a crystalline substance slightly soluble in water.

Citramic acid and citrimide are not known, but phenylic derivatives of these amides have been obtained.

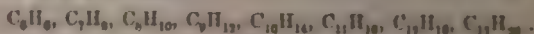
Benzene-Derivatives, or Aromatic Group.

The hydrocarbons, C_nH_{2n-6} , viz., benzene and its homologues, together with the alcohols, acids, and bases derived from them, form a group resembling the fatty bodies in many of their chemical relations, but nevertheless exhibiting decided peculiarities, which mark them as a natural family. They are called aromatic, on account of the peculiar and fragrant odors possessed by some of them, especially by certain derivatives of benzene, such as benzoic acid, bitter almond oil, etc.

Intimately related to these bodies are certain other hydrocarbons with their derivatives, containing proportionally smaller numbers of hydrogen atoms, namely: cinnamene C_8H_6 , naphthalene $C_{10}H_8$, anthracene $C_{14}H_{10}$, pyrene $C_{16}H_{10}$, and chrysene $C_{18}H_{12}$, and the terpenes, $C_{10}H_{14}$, which contain a larger number of hydrogen atoms than benzene and its homologues.

HYDROCARBONS, C_nH_{2n-6} .

This is the principal series of the aromatic group, analogous to the paraffin series in the fatty group. The known hydrocarbons belonging to it are represented by the formulae,



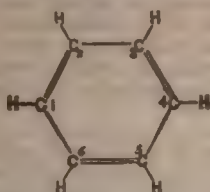
The first is called benzene; the second, toluene;* the others admit of isomeric modifications, the names of which will be given hereafter. Many of these hydrocarbons are found in the lighter part of the oil naphtha obtained by the destructive distillation of coal, and may be separated from one another by fractional distillation.

These hydrocarbons might be regarded as derived from the paraffins by abstraction of 8 atoms of hydrogen (e. g., $C_6H_6 = C_6H_{14} - H_8$), or from the olefines by abstraction of 6 atoms of hydrogen, etc., and accordingly

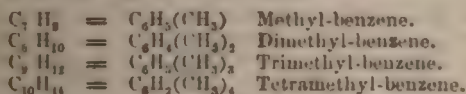
* Frequently also benzol, toluol, etc.; but it is not desirable to apply the same termination to hydrocarbons and their alcoholic derivatives.

they might be expected to act as octovalent, sexvalent, quadrivalent, or bivalent radicals; and, in fact, benzene does form definite compounds with 6 atoms of chlorine and of bromine. But in nearly all cases the aromatic hydrocarbons react as saturated molecules, like the paraffins, yielding, when treated with chlorine, bromine, or nitric acid, not additive compounds, but substitution-products.

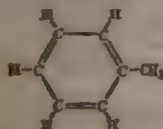
Benzene may be represented as a saturated molecule by the following constitutional formula, in which the carbon-atoms are united together by one or two combining units alternately:—



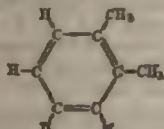
The other hydrocarbons of the series may be derived from it by successive additions of CH_2 , or by substitution of methyl, CH_3 , in the place of one or more of the hydrogen-atoms; thus:



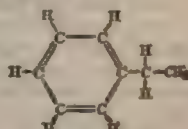
Further, a hydrocarbon isomeric with dimethyl-benzene may be formed by the substitution of ethyl, C_2H_5 , for 1 atom of hydrogen in benzene, viz., ethyl-benzene, $C_6H_5(C_2H_5)$; in like manner methyl-ethyl-benzene, $C_6H_4(CH_3)(C_2H_5)$, and propyl-benzene, $C_6H_5(C_3H_7)$, are isomeric with trimethyl-benzene; diethyl-benzene with tetra-methyl-benzene, etc. etc. It is easy to see that in this manner a large number of isomeric bodies may exist in the higher terms of the series. The structure of these isomeric hydrocarbons may be illustrated by the following figures:—



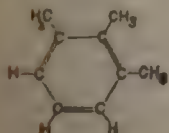
Methyl-benzene.



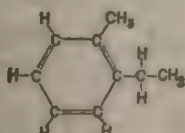
Dimethyl-benzene.



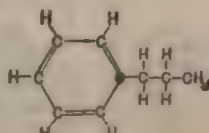
Ethyl-benzene.



Trimethyl benzene.



Methyl-ethyl-benzene.



Propyl-benzene.

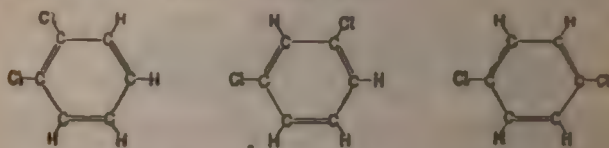
In these homologues of benzene, the six carbon-atoms belonging to the benzene itself are said to form the benzene-ring, benzene-nucleus, or principal chain, while the groups CH_3 , CH_2CH_3 , etc., joined on to

these carbon-atoms are called lateral chains. The chemical properties of an aromatic hydrocarbon differ considerably according to the number of lateral chains which it contains.

The replacement of the hydrogen-atoms in the principal and lateral chains by Cl, Br, NO_2 , OH, NH_2 , etc., gives rise to substitution-derivatives which exhibit numerous cases of isomerism.

I. In *Benzene-derivatives*.—The mono-derivatives of benzene do not exhibit isomeric modifications: thus there is but one monobromo-, mono-nitro-, or mono-amidobenzene, one monohydroxyl-derivative or phenol $C_6H_5(OH)$, etc. Hence it must be inferred that the molecule of benzene is perfectly symmetrical, all its six carbon-atoms and all its six hydrogen-atoms being equal to one another in value, and discharging similar functions, so that the replacement of a single hydrogen-atom by another element or radicle produces the same effect, in whatever part of the molecule the substitution takes place.

The higher derivatives, on the other hand, formed by replacement of two or more hydrogen-atoms in the molecule, exhibit isomeric modifications which are supposed to depend upon the relative positions, or orientation, of the substituted radicles. Referring to the figure on page 809 in which the carbon-atoms in benzene are numbered from one to six, it is easy to see that there may be three such modifications of dichlorobenzene, $C_6H_4Cl_2$, represented by the following figures:



These three modifications are distinguished by the symbols

1 : 2

1 : 3

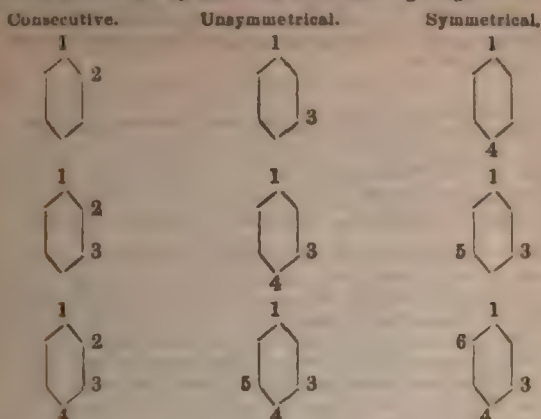
1 : 4

In the first the two chlorine-atoms are contiguous; in the second they are separated by one atom; and in the third by two atoms of hydrogen. It is clear that these are the only three modifications possible: for 2 : 3, 3 : 4, 4 : 5, and 5 : 6, would be the same as 1 : 2; 2 : 4 and 3 : 5 would be the same as 1 : 3; and 2 : 5 and 3 : 6 would be the same as 1 : 4.

The number of possible modifications formed by successive replacement of the hydrogen-atoms in benzene is as follows:

| Number of Hydrogen-atoms replaced. | Number of Modifications. | Positions of the replaced Hydrogen-atoms. | | |
|------------------------------------|--------------------------|---|----------------|--------------|
| one | one | 1, | | |
| two | three | 1, 2, | 1, 3, | 1, 4 |
| three | three | 1, 2, 3, | 1, 3, 4, | 1, 3, 5 |
| four | three | 1, 2, 3, 4, | 1, 3, 4, 5, | 1, 3, 4, 6 |
| five | one | 1, 2, 3, 4, 5, | | |
| six | one | | | |
| | | Consecutive. | Unsymmetrical. | Symmetrical. |

The meaning of the terms consecutive, symmetrical, and unsymmetrical, applied to the three modifications of the di-, tri-, and tetra-derivatives, will be better understood by means of the following diagram:—



By counting from different points of the hexagons it is easy to see that:

in the tri-derivatives, 1, 3, 4 is the same as 1, 2, 4, 1, 2, 5 and 1, 3, 6
 in the tetra-derivatives, 1, 3, 4, 5 " 1, 2, 3, 5, 1, 2, 4, 6 and 1, 3, 5, 6
 and 1, 3, 4, 6 " 1, 2, 4, 5.

B. The hydrogen-atoms are replaced by different elements or radicles.

If only two hydrogen-atoms are thus replaced, the number of possible modifications remains the same as above, viz., three; for the reversal of the order (AB or BA) can make no difference in the result; but if three or more hydrogen-atoms are replaced by different radicles, the number of possible modifications becomes larger, inasmuch as the order of succession of the substituted radicles may then exert an influence on the nature of the product; thus: to one tribromobenzene, $C_6Br_3H_3$, in which the bromine-atoms occupy the places 1, 2, 3, there will correspond two dibromochlorobenzenes, viz., $C_6Br_2ClH_4$, and $C_6BrCl_2H_4$.

In the present state of our knowledge we cannot in all cases assign to the several radicles which replace the hydrogen in benzene their exact relative positions in each isomeric modification; though so far as regards those derivatives in which the substituted radicles are all alike, the list is nearly complete; but inasmuch as a given modification of a benzene-derivative may in many cases be converted into a particular modification of another benzene-derivative, by simple transformations not likely to be attended by any change of molecular structure, we may conclude that in the two derivatives thus producible one from the other, the radicles which replace two or more atoms of hydrogen will occupy corresponding places. Accordingly, the derivatives of benzene containing a given number of replaced hydrogen-atoms may be divided into groups, each containing those modifications which can be formed one from the other, and in which therefore the radicles which have replaced the hydrogen-atoms may be supposed to be similarly situated.

The di-derivatives of benzene, e. g., $C_6H_4Cl_2$, C_6H_4ClBr , $C_6H_4Cl(NO_2)$, etc., exhibit, as above mentioned, three such modifications, which are distinguished by the prefixes *ortho*, *meta*, and *para*: thus the three dichlorobenzenes are designated as follows:—

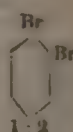
| | | | 1 | 2 | 3 | 4 | 5 | 6 |
|-----------------------------|---|---|---|-------|----|----|----|----|
| Orthodichlorobenzene, 1 : 2 | . | . | . | C_6 | Cl | Cl | H | H |
| Metadichlorobenzene, 1 : 3 | . | . | . | C_6 | Cl | H | Cl | H |
| Paradichlorobenzene, 1 : 4 | . | . | . | C_6 | Cl | H | H | Cl |

The following are the principal or typical representatives of these three series of compounds :—

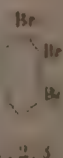
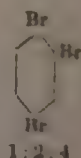
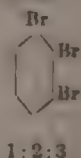
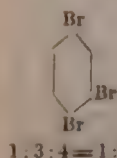
| | 1 : 2 | 1 : 3 | 1 : 4 |
|---|--|-------------|----------------|
| Dihydroxybenzenes } $C_6H_4(OH)_2$ or Oxyphenols, | Pyrocatechin | Resorcin | Hydroquinone |
| Oxy-acids, | $C_6H_4 \begin{smallmatrix} OH \\ CO_2H \end{smallmatrix}$ Salicylic | Oxybenzoic | Paraoxybenzoic |
| Dimethyl-benzenes, $C_6H_4(CH_3)_2$ | Orthoxylene | Metaxylene | Paraxylene |
| Dicarbon-acids, $C_6H_4(CO_2H)_2$ | Phthalic | Isophthalic | Terephthalic |

The relative positions of the substituted radicles in a di-derivative of benzene may be determined by comparison with those in the tri-derivatives which may be formed from it or converted into it. The principle of the method may be illustrated by the case of the di-bromobenzenes, $C_6H_4Br_2$. These, by the action of nitric acid, may be converted into six different nitrodibromobenzenes, $C_6H_3Br_2(NO_2)$; these latter, treated with reducing agents, yield the six corresponding amido-dibromobenzenes, $C_6H_3Br_2NH_2$, in which the NH_2 takes the place of the NO_2 ; and the amido-dibromobenzenes (dibromanilines), treated by processes hereafter to be described, exchange their NH_2 for H, whereby they are reconverted into dibromobenzenes, and for Br, whereby they yield tribromobenzenes. The relations between these di- and tri-derivatives are shown in the following diagram, in which, for simplicity, the C's and H's of the benzene-molecule are omitted, and only the substituted radicles are shown in their relative places, the several tribromo- and nitrodibromobenzenes are placed vertically under the dibromobenzenes from which they are derived.

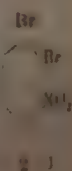
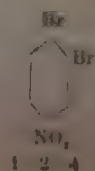
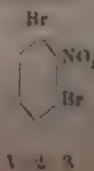
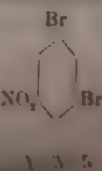
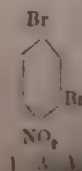
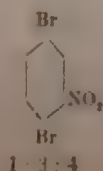
Dibromobenzenes.



Tribromobenzenes.



Nitrodibromobenzenes.



An inspection of this diagram shows : (1) That a para-derivative (1 : 4) can give rise to, or be derived from, only *one* tri-derivative, viz., the unsymmetrical modification, 1 : 2 : 4 or 1 : 3 : 4.

(2) That an ortho-derivative (1 : 2) can give rise to, or be produced from, *two* tri-derivatives, viz., the consecutive 1 : 2 : 3, and the unsymmetrical 1 : 2 : 4.

(3) That a meta-derivative (1 : 3) can give rise to, or be formed from, *all* the three tri-derivatives, 1 : 2 : 3, 1 : 3 : 4, and 1 : 2 : 4.

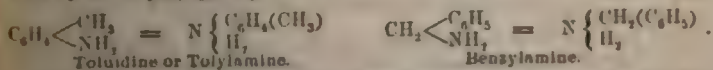
These conclusions, which are fully borne out by experiment, enable us to give definitions of the three classes of di-derivatives depending only on their relations to the tri-derivatives, and independent of all assumptions as to the relative positions of the substituted radicles ; thus :

A di-derivative of benzene is para-, ortho-, or meta-, according as it can give rise to, or be formed from, one, two, or three tri-derivatives.

II. *In the Substitution-derivatives of the Homologues of Benzene.*—The derivatives of toluene and the higher hydrocarbons of the series C_nH_{2n-6} , exhibit two kinds of isomerism : (1) According as the replacement of the hydrogen takes place in the benzene-nucleus or principal chain, or in one of the lateral chains (p. 809); thus from toluene, $C_6H_5.CH_3$, are derived :

| | | |
|---------------------------------------|---------------|--------------------------------------|
| $C_6H_4Cl.CH_3$
Monochlorotoluene. | isomeric with | $C_6H_5.CH_2Cl$
Benzyl chloride. |
| $C_6H_4(OH).CH_3$
Cresol. | " | $C_6H_5.CH_2(OH)$
Benzyl alcohol. |
| $C_6H_4(NH_2).CH_3$
Toluidine. | " | $C_6H_5.CH_2(NH_2)$
Benzylamine. |

These isomeric derivatives differ considerably from one another in their properties. Those in the left-hand column, formed by replacement of hydrogen in the benzene-nucleus, like those derived in like manner from benzene itself,—are comparatively stable compounds, which do not give up their chlorine, hydroxyl, etc., in exchange for other radicles so easily as the corresponding derivatives of the paraffins,—whereas those in the right-hand column, formed by replacement of hydrogen in the lateral chain, are more active bodies, easily susceptible of this kind of transformation. Thus benzyl alcohol treated with hydrochloric acid yields benzyl chloride (just as ordinary ethyl alcohol similarly treated yields ethyl chloride), and this compound heated with ammonia yields benzylamine; the chloride is also easily converted into the acetate, cyanide, etc., by treatment with the corresponding potassium salts. In short, these last-mentioned toluene derivatives exhibit reactions exactly like those of the corresponding compounds of the methyl and ethyl groups. The two series of compounds may, however, be represented by formulae of similar structure, but containing isomeric radicles, C_6H_7 , those in the left-hand column being compounds of methyl-phenyl or tolyl, $C_6H_4(CH_3)$, and those in the right-hand column being compounds of phenyl-methyl or benzyl, $CH_2(C_6H_5)$; e. g. :

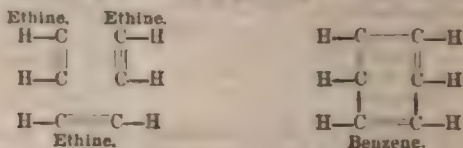


(2) According to the orientation of the substituted radicles in the benzene-nucleus.—This kind of isomerism is of course exhibited only by derivatives like those in the left-hand column, including the hydrocarbons which contain more than one lateral chain; thus: dimethyl-benzene or xylene, $C_6H_4(CH_3)_2$, exhibits the three modifications, 1 : 2, 1 : 3, and 1 : 4.

The difference in chemical character arising from substitution in the principal or in the lateral chains is much greater than that which depends on the orientation of the substituted radicles in the principal chain; in fact, the differences in the latter case are chiefly of physical character, relating to density, melting point, boiling point, etc. In speaking of these two kinds of modification, it will be convenient to designate the former as metameric, the latter as isomeric.

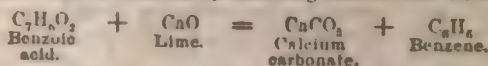
Benzene, C_6H_6 .—This hydrocarbon can be produced synthetically from its elements. When ethine or acetylene, C_2H_2 , which, as we have seen (p. 510), may be formed by the direct combination of carbon and hydrogen, is heated to a temperature somewhat below redness, it is converted into several polymeric modifications, the principal of which is triethine or benzene, $3C_2H_2 = C_6H_6$.

This mode of formation leads at once to the constitutional formula of benzene above given: for suppose three molecules of ethine placed as in the left-hand figure below; and, further, that one of the three units of affinity between the two carbon-atoms in each of these molecules is removed, and employed in linking together the alternate carbon-atoms: then we have the formula of benzene, as given in the right-hand figure.



Benzene is also formed in the dry distillation of many organic substances, and is contained in considerable quantity in the more volatile portion of coal-tar oil, from which it is now almost always prepared. To obtain it, the oil is repeatedly washed with dilute sulphuric acid and with potash, to remove the alkaline and acid products likewise existing in it; and the remaining neutral oil is submitted to repeated fractional distillation, the portion which goes over between 80° and 90° C. (176° – 194° F.) being collected apart. On cooling this distillate to -12° C. (10.4° F.), the benzene crystallizes out, and may be purified from adhering liquid substances by pressure. It is now prepared in immense quantities for the manufacture of aniline; but the commercial product is always impure, containing also the higher members of the series.

Pure benzene may be obtained by distilling benzoic acid with lime:



Benzene is identical with the so-called *bicarburet of hydrogen*, discovered many years ago by Faraday in the liquid condensed during the compression of oil-gas (p. 166).

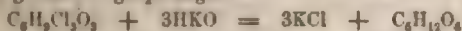
Pure benzene is a thin, limpid, colorless, strongly refracting liquid, having a peculiar etheral odor. It has a density of 0.889 at 0° , 0.885 at 15.5° C. (59.9° F.), boils at 80.5° C. (176.9° F.), and solidifies at 0° to a mass of rhombic crystals melting at 3° C. (37.4° F.). It is nearly insoluble in water, but mixes with alcohol and ether. It dissolves iodine, sulphur, and phosphorus, and a large number of organic substances, fats and resins for example, which are insoluble, or very sparingly soluble, in water and

sol: hence its use in many chemical preparations, and for removing oil-spots from articles of dress.

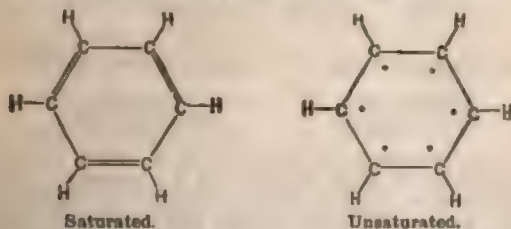
Benzene, passed in the state of vapor through a porcelain tube heated to a bright redness, is partly resolved into hydrogen gas containing a small quantity of ethine, and the following liquid products: (1) diphenyl, $C_{12}H_{10} = 2C_6H_5 - H_2$; (2) diphenyl benzene, $C_6H_5(C_6H_5)_2$, formed according to the equation $3C_6H_6 = C_{18}H_{14} + 2H_2$; (3) benzerythrene, a solid, resinous, orange-colored body of unknown composition, which dissolves in yellow vapors at a dull red heat; (4) bitumene, a blackish solid, which remains in the retort at a dull red heat, and solidifies on cooling.* Heated to 275°C .– 280°C . (527°F .– 536°F .) with 80 to 100 parts of dry hydriodic acid, it is converted into hexane, C_6H_{14} .

ADDITIVE COMPOUNDS OF BENZENE.—Benzene, though, as already observed, mostly reacts as a saturated molecule—exhibiting indeed in its chemical actions a very close resemblance to the paraffins—can nevertheless, under certain circumstances, take up 6 atoms, or 3 molecules, of chlorine or bromine, forming the compounds $C_6H_6Cl_6$ and $C_6H_6Br_6$. These are crystalline solids, obtained by exposing benzene to sunshine in contact with chlorine or bromine, the former also by mixing the vapor of boiling benzene with chlorine. Benzene hexachloride melts at 132°C . (269.6°F .), and boils at 171°C . (350.4°F .), being partly resolved at the same time into hydrochloric acid and trichlorobenzene: $C_6H_6Cl_6 = 3HCl + C_6H_3Cl_3$. The same composition is quickly produced by heating the compound with alcoholic solution of potash. Benzene hexbromide exhibits a similar reaction.

Benzene is also capable of uniting directly with three molecules of *hypobromous acid*, forming the compound $C_6H_6Cl_3O_3$, or $C_6H_6.3ClO_2H$, which crystallizes in thin colorless plates melting at about 110° , and is converted by fusion into a white deliquescent compound called *phenose*, $C_6H_{12}O_6$, isomeric with glucose or grape-sugar:

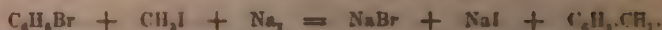


The formation of these additive compounds may be explained in the same manner as that of ethene bromide (pp. 504–5), namely, by supposing that the benzene-molecule is subjected to the influence of chlorine, bromine, etc., the attachment of the alternate pairs of carbon-atoms is effected, so that each pair of carbon-atoms becomes united by only one unit of affinity, and each carbon-atom has one unit of affinity left free, ready to take up an atom of chlorine or other univalent radicle. The effect of the alteration is shown by the following figures, in the second of which the unsaturated affinities are indicated by dots:

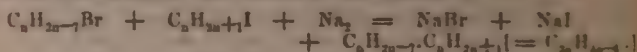


toluene, C_7H_8 , or **Methyl-benzene**, $C_6H_5(CH_3)$.—This hydrocarbon is produced: Synthetically (1) By the action of sodium on a mixture of bromobenzene (phenyl bromide), and methyl iodide:

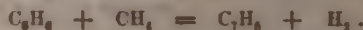
Berthelot, Bulletin de la Société Chimique de Paris [2], vi. pp. 272, 270; 1872, Ann. Chem. clixiv. 201.



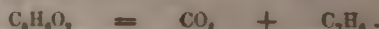
This reaction is an example of a general synthetical method of producing the hydrocarbons C_nH_{2n-6} , represented by the equation:



2. By the mutual action of benzene and methane in the nascent state as when a mixture of 2 parts of sodium acetate and 1 part of sodium benzoate is subjected to dry distillation:



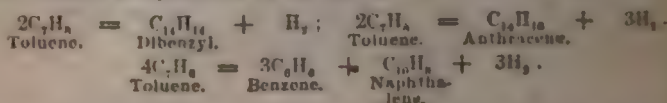
It is also produced by distilling toluic acid, $C_8H_7O_2$, with lime, which abstracts carbon dioxide:



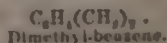
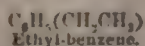
It occurs, together with benzene and the other hydrocarbons of the series in light coal-tar oil, and in the products of the distillation of wood, Tolu balsam, dragon's blood, and other vegetable substances, and together with many other hydrocarbons, in Rangoon tar or Burmese naphtha.

Toluene is a limpid liquid, smelling like benzene, and having a density of 0.862 at 0° . It boils at $111^\circ C.$ ($231.8^\circ F.$), and does not solidify at $-20^\circ C.$ ($-4^\circ F.$). In respect of solubility and solvent power, it is very much like benzene, but dissolves somewhat more readily in alcohol. When treated with oxidizing agents, it yields benzoic acid, $C_7H_5O_2$, and derivatives thereof; with potassium chromate and sulphuric acid, it yields benzoic acid; and by prolonged boiling with strong nitric acid, nitrotoluic acid.

Toluene vapor passed through a red-hot porcelain tube is partly resolved into hydrogen gas (with small quantities of methane and ethine), and the following liquid products: (1) Benzene and naphthalene in considerable quantities. (2) A crystallizable hydrocarbon volatilizing at $286^\circ C.$ ($546^\circ F.$), and probably consisting of dibenzyl, $C_{14}H_{14}$. (3) A liquid isomer with the last. (4) A mixture, distilling above $360^\circ C.$ ($682^\circ F.$), of is-thracene with an oily liquid. (5) Chrysene and the last decomposes the products of benzene. The formation of benzene, naphthalene, anthracene, and dibenzyl is represented by the equations:



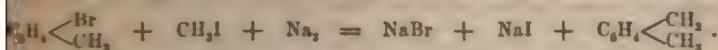
Hydrocarbons, C_nH_{10} .—This formula includes the two metameric bodies:



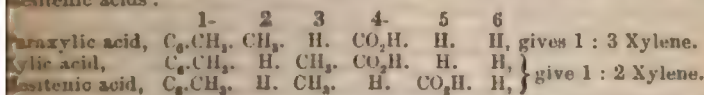
1. **ETHYL-BENZENE** is produced by the action of sodium on a mixture of monobromobenzene and ethyl bromide. It is a colorless, mobile liquid very much like toluene, having a density of 0.866, and boiling at $144^\circ C.$ ($273.2^\circ F.$). By oxidation with chromic acid mixture it yields benzoic acid. It is attacked by chlorine, bromine, and nitric acid, forming substitution-products.

2. **DIMETHYL-BENZENE, or XYLENE**, admits of the three modifications para-, ortho-, and meta. The first and second are produced by the action

of sodium on a mixture of methyl iodide with para- and ortho-bromotoluene respectively, the bromine-atom in each case being replaced by methyl:

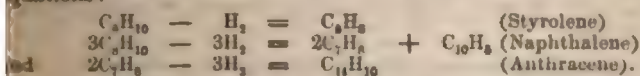


Orthoxylene is also formed by heating orthodimethyl-benzoic acid, $C_8H_{10}O_2 = C_6H_4 \begin{smallmatrix} (CH_3)_2 \\ \diagup \diagdown \\ CO_2H \end{smallmatrix}$, (inappropriately called paraxylic acid), with lime; $C_8H_{10}O_2 = CO_2 + C_8H_{10}$, and metaxyylene (or isoxylene) in like manner from two other modifications of the same acid called xylic and mesitenic acids:

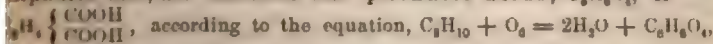


These isomeric xylenes are colorless, volatile liquids, orthoxylene boiling at 140° – 141° C. (284° – 285.8° F.), metaxyylene at 137° C. (278.6° F.), and paraxyylene at 136° – 137° C. (276.8° – 278.6° F.). Meta- and para-xylene are contained in the less volatile portion of light coal-naphtha. When the portion of this liquid which boils at about 141° C. (285.8° F.) is shaken with oil of vitriol containing a little fuming sulphuric acid, the xylene is dissolved in the form of xylene-sulphonic acid, $C_8H_{10}SO_3$; and by decomposing this compound by dry distillation, and purifying the distillate by washing, drying, and rectification, a mixture of metaxyylene and paraxyylene is obtained, containing 90 per cent. of the former.

Xylene (either modification) passed through a red-hot tube, is resolved into a mixture of several hydrocarbons, among which are benzene, toluene, styrolene, naphthalene, anthracene, and its higher homologues. The formation of some of these products is represented by the following equations:

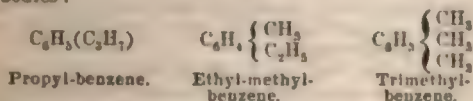


The xylenes, oxidized with a mixture of potassium dichromate and sulphuric acid, are converted into phthalic acids, $C_8H_6O_4$, or

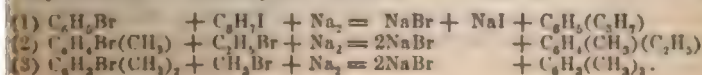


each modification of the hydrocarbon yielding a corresponding modification of the acid.

Hydrocarbons, C_9H_{12} .—This formula includes the three following isomeric bodies:



All three have been formed synthetically, the first by the action of sodium and propyl iodide on bromobenzene; the second by that of sodium and ethyl bromide on bromotoluene; the third by that of sodium and methyl bromide on bromoxylene; thus:



1. **Propyl-benzene** is a liquid which boils at 157°C . (314.6°F .), forms with excess of bromine a viscid tetrabrominated compound, $C_9H_5Br_4$, and with excess of strong nitric and sulphuric acids, a crystalline trinitro-derivative, $C_9H_5(NO_2)_3$.

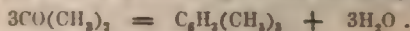
A hydrocarbon, called **cumene**, also having the composition C_9H_{10} , and very much like propyl-benzene, exists ready formed in Roman cum-oil, and is obtained artificially by distilling cumic acid, $(C_{10}H_{12}O)_2$, with lime; but it boils at a lower temperature, viz., 151°C . (303.8°F .), forms with bromine a finely crystallized pentabrominated derivative, $C_9H_7Br_5$, and is converted by excess of a mixture of nitric and sulphuric acids only into dinitrocumene, $C_9H_{10}(NO_2)_2$. It agrees with propyl-benzene, however, in being converted by oxidation with chromic acid into benzoic acid. Hence it is probable that both these hydrocarbons have the composition $C_6H_5.C_3H_7$; but that cumene consists of *isopropyl-benzene*, $C_6H_5.CH(CH_3)_2$, whereas the compound formed by the action of sodium and propyl iodide on bromobenzene is *normal propyl-benzene*, $C_6H_5.CH_2CH_2CH_3$. This supposition is in accordance with the lower boiling point of cumene, as it is a general rule that isopropyl-compounds boil at lower temperatures than the corresponding normal propyl-compounds.

Cumene dissolves in hot fuming nitric acid, and water added to the solution throws down a heavy oil, consisting of mononitrocumene, $C_9H_{11}(NO_2)$, which is reduced by ammonium sulphide to amidocumene or cumidine, $C_9H_{11}(NH_2)$.

2. **ETHYL-METHYL-BENZENE** or **ETHYL-TOLUENE** is known in two isomeric modifications. The *para*-modification (1 : 4), obtained from parabromotoluene and ethyl bromide in the same manner as ethyl-benzene from bromobenzene, is a liquid boiling at $161\text{--}162^{\circ}\text{C}$. ($321.8\text{--}323.6^{\circ}\text{F}$.), and having a density of 0.865 at 21°C . (69.8°F .). By oxidation it yields terephthalic acid. The *meta*-modification (1 : 3), obtained in like manner from metabromotoluene, boils at $158\text{--}159^{\circ}\text{C}$. ($316.4\text{--}318.2^{\circ}\text{F}$.); has a density of 0.869 at 20°C . (68°F .); and is converted by oxidation into isophthalic acid.

3. **TRIMETHYL-BENZENE**, $C_6H_3(CH_3)_3$, is susceptible of three isomeric modifications, only two of which, however, are known. Both of them exist in coal-tar, but cannot be completely separated therefrom by fractional distillation.

Mesitylene, or **Symmetrical Trimethyl-benzene**, $C_6H_3.H.CH_3.H.CH_3.H$, is formed by distilling acetone with sulphuric acid:



A mixture of 1 vol. acetone and 1 vol. sulphuric acid, diluted with $\frac{1}{2}$ vol. water, is distilled from a retort containing sand, and the oily layer of the distillate is separated from the watery layer, washed with solution of sodium carbonate, and distilled.

Mesitylene is a colorless, fragrant liquid, boiling at 163°C . (325.4°F .). By oxidation with dilute nitric acid, it is successively converted into mesitylenic acid, $C_6H_3(CH_3)_3CO_2H$, mesidic or nvtic acid, $C_6H_3(CH_3)_3(COOH)_2$, and trimesic acid, $C_6H_3(COOH)_3$, all of which have the symmetrical structure 1 : 3 : 5. By oxidation with chromic acid mixture it is completely decomposed, with formation of acetic acid. Heated with phosphonium iodide, PIH_4 , to $250\text{--}300^{\circ}\text{C}$. ($482\text{--}572^{\circ}\text{F}$.), it is converted into the hydrocarbon, C_9H_{10} , which boils at 136°C . (276.8°F .), and yields, with oxidizing agents, the same products as mesitylene itself.

Pseudocumene or Unsymmetrical Trimethyl-benzene, $C_6H_5 \cdot CH_3 \cdot H \cdot CH_3 \cdot CH_3 \cdot H_2$, occurs, together with mesitylene, in coal-tar oil (boiling at 162° – 168° C.) (323.6° – 334.4° F.), and is formed by the action of methyl iodide and sodium on bromoparaxylene, $C_6H_4 \cdot H \cdot Br \cdot CH_3 \cdot H_2$, or bromometaxylene, $C_6H_4 \cdot H \cdot CH_3 \cdot Br \cdot H_2$. It boils at 166° C. (330.8° F.), and is oxidized by dilute nitric to paraxylic acid, $C_6H_5(CH_3)_2CO_2H$, and xylic acid, $C_6H_3(CH_3)(CO_2H)_2$.

Hydrocarbons, $C_{10}H_{16}$.—Of these there are five metameric modifications, viz. :—

| | |
|----------------------------------|--------------------------------------|
| Butyl-benzene | $C_6H_5 \cdot C_4H_9$ |
| Methyl-propyl-benzene | $C_6H_4 \cdot CH_3 \cdot C_3H_7$ |
| Diethyl-benzene | $C_6H_4 \cdot C_2H_5 \cdot C_2H_5$ |
| Ethyl-dimethyl-benzene | $C_6H_3 \cdot C_2H_5 \cdot (CH_3)_2$ |
| Tetramethyl-benzene | $C_6H_2(CH_3)_4$ |

1. **BUTYL-BENZENE**.—Of this hydrocarbon there are three submodifications depending upon the structure of the butyl-radicle. *Normal butyl-benzene*, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$, and *Isobutyl-benzene*, $C_6H_5 \cdot CH_2 \cdot CH(CH_3)_2$, are obtained by the action of sodium on a mixture of bromobenzene and normal or isobutyl bromide, or on a mixture of benzyl bromide ($C_6H_5 \cdot CH_2Br$), or chloride, with the iodide of normal propyl or isopropyl. The first has a density of 0.8622 at 16° C. (60.8° F.), and boils at 180° C. (356° F.); the second has a density of 0.89 at 15° C. (59° F.), and boils at 167.5° C. (333.5° F.). A third *butyl-benzene*, $C_6H_5 \cdot CH \begin{smallmatrix} CH_3 \\ | \\ CH_2CH_3 \end{smallmatrix}$, having a density of 0.8726 at 16° C. (60.8° F.), and boiling at 170° – 172° C. (338° – 341.6° F.), is produced by the action of zinc-ethyl on phenyl-ethyl bromide, $C_6H_5 \cdot CHBr \cdot CH_2CH_3$.

2. **METHYL-PROPYL-BENZENE OR CYMENE**, $C_6H_4 \begin{smallmatrix} CH_3 \\ | \\ CH_2CH_2CH_3 \end{smallmatrix}$ (1 : 4), occurs in Roman cumin oil (the volatile oil of the seeds of *Cuminum Cuminum*), and in the volatile oils of *Ptychotis Ajoowan*, *Cicuta virosa*, *Eucalyptus globulus*, and other plants. It is produced synthetically by the action of sodium on a mixture of parabromotoluene and normal propyl iodide; formed also from turpentine oil and its isomerides, $C_{10}H_{16}$, by heating with iodine, by the action of strong sulphuric acid, and by heating the dibromides of these hydrocarbons with sodium, alcoholic potash, or aniline. It appears also to be formed in small quantity by the spontaneous oxidation of turpentine oil in contact with the air. Further, it is produced from the isomeric compounds, thymol and carvacrol, $C_6H_3(OH)(CH_3)(C_2H_5)$, by heating with phosphorus pentasulphide, or by the action of phosphorus pentachloride and sodium-amalgam, chlorocymene being first produced and then dechlorinated by the sodium-amalgam; lastly, together with toluene, xylene, mesitylene, and other hydrocarbons, by distilling camphor, $C_{10}H_{16}O$, over zinc chloride or phosphoric anhydride. It is most easily prepared by gently heating two parts of camphor with one part of phosphorus pentasulphide, repeatedly agitating the crude distillate with strong sulphuric acid, and rectifying.

Cymene is a liquid having a specific gravity of 0.8732 at 60° , and boiling at 175° C. (347° F.). By oxidation with nitric and with chromic acid, it yields paratoluic and terephthalic acids. It dissolves in strong sulphuric acid, forming a sulphonic acid, the barium salt of which crystallizes in shining laminae, having the composition $(C_{10}H_{15}SO_3)_2Ba + 3H_2O$.

3. **DIETHYL-BENZENE**, $C_6H_4(C_2H_5)_2$ (1 : 4), obtained by the action of sodium on a mixture of bromethyl-benzene and ethyl bromide, is a color-

less liquid which boils at 178° – 179° C. (352.4° – 354.2° F.), and is converted by oxidation into ethyl-benzoic acid (1 : 4) and terephthalic acid.

4. ETHYL-DIMETHYL-BENZENE or ETHYL-XYLENE, C_8H_{10} , $\left\{ \begin{smallmatrix} C_2H_5 \\ (CH_3)_2 \end{smallmatrix} \right.$, together with methyl-diethyl-benzene, by distilling a mixture of acetone (acetone) and methyl-ethyl ketone with sulphuric acid, like mesitylene, it possesses the symmetrical structure, 1 : 3 : 5. It has a density of 0.864 at 20° C. (68° F.), boils at 180° – 182° C. (359.6° – 359.6° F.), and is oxidized by nitric acid to mesitylene and oxalic acid.

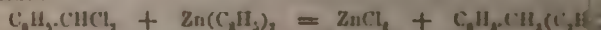
5. TETRAMETHYL-BENZENE or DURENE, C_8H_{10} , $(CH_3)_4$, (consecutive metrical ?), is formed by the action of sodium on a mixture of iodide and bromopseudocumene on dibromoxylene. It is crystalline at ordinary temperatures, melts at 73 – 80° C. (174.2° – 176° F.), boils at 190° C. (374° F.), and is oxidized by dilute nitric acid to durene, $C_8H_2(CH_3)_4CO_2H$, and cumidic acid, $CH(CH_3)_2(CO_2H)_2$.

The unsymmetrical modification (1 : 3 : 4 : 5), obtained from mesitylene, boils at 192° – 194° C. (377.6° – 381.2° F.), and remains liquid at low temperatures.

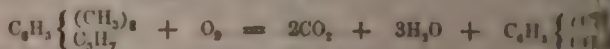
Hydrocarbons, $C_{11}H_{16}$.—Of the seven metameric compounds presented by this formula, three only have been obtained, viz.:

| | | |
|---|---|---|
| Amyl-benzene | $C_6H_5.C_5H_{11}$ | boiling at 193° C. (379° F.) |
| Diethyl-methyl-benzene, or
Diethyl-toluene | $C_6H_5 \left\{ \begin{smallmatrix} CH_3 \\ (C_2H_5)_2 \end{smallmatrix} \right.$ | " 176° C. (346° F.) |
| Propyl-dimethyl-benzene,
Propyl-xylene or Laurene | $C_6H_5 \left\{ \begin{smallmatrix} (CH_3)_2 \\ C_3H_7 \end{smallmatrix} \right.$ | " 188° C. (370° F.) |

The first is obtained by the action of sodium on a mixture of methyl-benzene and amyl bromide; the second by that of zinc-ethyl on benzene chloride:



the third, together with several of its lower homologues, by heating camphor with zinc chloride. The constitution of this last modification is inferred from its reaction with dilute nitric acid, which oxidizes lauroxylic acid, $C_9H_{10}O_2$:



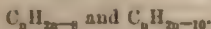
Hydrocarbons, $C_{12}H_{18}$ and $C_{12}H_{16}$.—These bodies admit of various modifications, but the first is known in only two, the asymmetric modification, viz.:

| | | Boiling point. | Specific gravity. |
|---|--|--|-------------------|
| Triethyl-benzene | $C_6H_5(C_2H_5)_3$ | 218° C. (424.4° F.) | |
| Amyl-methyl-benzene or
Amyl-toluene | $C_6H_5 \left\{ \begin{smallmatrix} C_5H_{11} \\ CH_3 \end{smallmatrix} \right.$ | 213° C. (415.4° F.) | |
| Amyl-dimethyl-benzene or
Amyl-xylene | $C_6H_5 \left\{ \begin{smallmatrix} C_5H_{11} \\ (CH_3)_2 \end{smallmatrix} \right.$ | 233° C. (451.4° F.) | |

Triethyl-benzene (1 : 3 : 5) is formed by distilling ethyl-methyl ketone, $CH_3-CO-C_2H_5$, with sulphuric acid; it is oxidized by nitric acid to trimelic acid.

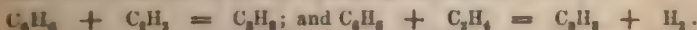
Amyl-methyl-benzene and amyl-dimethyl-benzene are formed by the action of sodium and amyl bromide on bromotoluene and bromoxylene respectively.

UNSATURATED HYDROCARBONS,



Ethenyl-benzene or **Vinyl-benzene**, $C_6H_5 = C_6H_5 - CH = CH_2$; also called *Phenyl-ethene*, *Cinnamene*, and *Styrolene*. This hydrocarbon occurs in liquid storax (from *Liquidambar orientale*), and may be prepared therefrom by distilling the balsam with water containing a little sodium carbonate, to retain cinnamic acid.

It is produced: 1. Synthetically: a. By passing a mixture of benzene-vapor and acetylene or ethene through a red-hot tube:



b. In like manner, together with benzene, from diphenyl and ethene:



2. In the decomposition of xylene which takes place when the vapor of that compound is passed through a red-hot tube: $C_{10}H_{10} = C_8H_8 + H_2$ (p. 817).

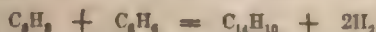
3. By distilling cinnamic acid with baryta, which removes carbon dioxide: $C_9H_8O_2 = CO_2 + C_8H_6$.

Cinnamene is a very mobile, colorless oil of specific gravity 0.924. It boils at $146^\circ C.$ ($294.8^\circ F.$), and has a density of 0.924. When heated to $200^\circ C.$ ($392^\circ F.$) in a sealed tube, it is converted into a white, transparent, highly refractive, solid substance, called *metacinnamene* or *metastyrolene*. This substance, when heated in a small retort, yields a distillate of pure liquid cinnamene.*

A mixture of cinnamene vapor and ethene passed through a red-hot tube yields large quantities of benzene and naphthalene. The first is produced from the cinnamene by abstraction of C_3H_3 ; the second according to the equation:



A mixture of cinnamene and benzene vapors, passed through a red-hot porcelain tube, yields anthracene, $C_{14}H_{10}$, together with small quantities of other products:



Cinnamene acts with chlorine and bromine like a bivalent radicle, forming the compounds $C_8H_7Cl_2$ and $C_8H_7Br_2$, which, when treated with alcoholic potash, give up HCl and HBr (like the corresponding ethene-compounds), leaving chloro-cinnamene, C_8H_7Cl , and bromocinnamene, C_8H_7Br . According to Laurent, cinnamene yields with chlorine a hexachloride of dichloro-cinnamene, $C_6H_4Cl_2 \cdot Cl_2$.—Metacinnamene is also acted upon by bromine, but with considerable difficulty.—Both cinnamene and metacinnamene treated with fuming nitric acid yield mononitrated derivatives, $C_8H_7(NO_2)$: that obtained from cinnamene is crystalline; that from metacinnamene amorphous.

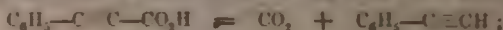
Allyl-benzene, $C_9H_{10} = C_6H_5 - CH_2 - CH = CH_2$, or *Phenylallyl*, formed by heating bromobenzene (phenyl bromide), C_6H_5Br , and allyl bro-

* It was formerly supposed that cinnamene prepared from cinnamic acid was not converted by heat into a solid modification, like styrolene from storax: hence the two were regarded as isomeric, not identical; but later researches have shown that pure cinnamene from cinnamic acid is likewise convertible into solid metacinnamene.

mide, C_6H_5Br , with zinc, boils at $155^\circ C.$ ($311^\circ F.$), and forms a dibromide melting at $60^\circ C.$ ($140^\circ F.$).

Phenyl-propylene, $C_6H_5-CH=CH-CH_3$, isomeric with it, is obtained from cinnamic alcohol; it boils at $170^\circ C.$ ($338^\circ F.$), and forms a dibromide melting at $66^\circ C.$ ($150.8^\circ F.$).

Acetenyl-benzene or Phenylacetylene, $C_6H_5-C\equiv CH$, is formed by heating bromocinnamene, $C_6H_5-CH=CHBr$, or acetophenone chloride, C_6H_5-COCl , with alcoholic potash; also by heating phenylpropionic acid to $120^\circ C.$ ($248^\circ F.$), with water or with baryta:



further, together with cinnamene, by the action of heat on several hydrocarbons. It is an aromatic liquid, boiling at $140^\circ C.$ ($284^\circ F.$), and precipitating ammoniacal silver and copper solutions, like acetylene. The copper-compound, $(C_6H_5)_2Cu$, is yellow; the silver-compound, $(C_6H_5)_3Ag$, is white. Sodium dissolves in it, forming the compound, C_6H_5Na , which takes fire on coming in contact with the air, and is converted by carbonic acid passed into its ethereal solution, into the sodium salt of phenylpropionic acid.

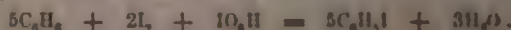
On shaking up the copper-compound with alcoholic ammonia, *diacetyphenyl*, $(C_6H_5)_2C_2H_2$ or $CH_3-C\equiv C-C_6H_5-C\equiv CH$, separates out. The compound, isomeric with pyrene, melts at $97^\circ C.$ ($206.6^\circ F.$), and forms a crystalline compound with picric acid.

Ethyl-acetenyl-benzene, $C_{10}H_{10} = C_6H_5-C\equiv C-C_2H_5$, obtained by the action of ethyl iodide on the sodium-compound of acetenyl benzene, is a colorless liquid having a density of 0.923 at $21^\circ C.$ ($69.8^\circ F.$), and boiling at $201-203^\circ C.$ ($393.8-397.4^\circ F.$).

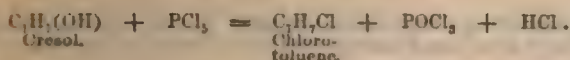
HALOGEN DERIVATIVES OF BENZENE AND ITS HOMOLOGUES.

These compounds are formed: (1) By direct substitution of the halogen elements. Chlorine and bromine act on the aromatic hydrocarbons more readily than on the paraffins, especially in presence of iodine, which acts as a carrier of the chlorine or bromine. The action of chloring is further promoted by the presence of a small quantity of antimony pentachloride, or molybdenum pentachloride, these bodies first giving up a portion of their chlorine to the hydrocarbon, whereby they are reduced to lower chlorides, which then take up an additional quantity of chlorine, and transfer it in like manner.

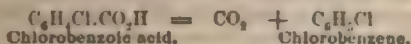
Iodine-derivatives cannot be obtained by the action of iodine alone, because, as in the case of the iodo-paraffins (p. 514), the substitution-product, if formed, would be immediately decomposed by the hydriodic acid formed at the same time. The reverse action may, however, be prevented by addition of iodic acid, the action taking place as represented by the equation:



(2) By the action of pentachloride, pentabromide, or pentaiodide of phosphorus on the hydroxyl-derivatives of the hydrocarbons (phenols and alcohols): e. g.,



(3) By the decomposition of substituted aromatic acids by heat; e. g.,



(4) The halogen-derivatives of benzene may be formed from amidobenzene, $\text{C}_6\text{H}_5\text{NH}_2$ (aniline), and the chloranilines, etc., $\text{C}_6\text{H}_4\text{Cl.NH}_2$, for example, by exchange of the group NH_2 for Cl , Br , etc., through the medium of the corresponding diazo-compounds (q. v.). This is a very important reaction, serving in many cases to determine the orientation of the halogen-atoms in the di-, tri-, and tetra-derivatives.

Benzene-derivatives.

Chlorobenzenes.—Of these compounds all the possible modifications have been obtained.

Monochlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$, or *Phenyl chloride*, prepared by chlorination of benzene, or by the action of PCl_5 on phenol, is a liquid of specific gravity 1.128 at 0° , boiling at 132°C . (269.6°F .), solidifying at -40°C . (-40°F .).

Dichlorobenzenes, $\text{C}_6\text{H}_4\text{Cl}_2$.—In the formation of these bodies by direct chlorination of benzene, the ortho- and para-modifications are always formed in preference to the meta; in fact the latter can, for the most part, be obtained only by indirect methods, as by exchange of the NH_2 in chloraniline for Cl in the manner above mentioned. The same observation applies to the dibromobenzenes.

Ortho- (1 : 2).—From benzene and chlorine (together with 1 : 4), and from orthochlorophenol. Colorless liquid, not solidifying at -19°C . (-2.2°F .). Boiling point 179°C . (354.2°F .); specific gravity = 1.3728 at 0° .

Meta- (1 : 3).—From metachloraniline, $\text{C}_6\text{H}_4\text{NH}_2\text{H.Cl.H}_3$, by exchange of NH_2 for Cl , and from dichloraniline (1 : 2 : 4), $\text{C}_6\text{H}_3\text{NH}_2\text{Cl.H.Cl.H}_3$, by exchange of NH_2 for H . Liquid, solidifying at -18°C . (0.4°F .), boiling at 175°C . (341.6°F .). Specific gravity 1.307 at 0° .

Para- (1 : 4), the chief product of the action of chlorine on benzene, in presence of iodine, forms colorless, monoclinic crystals, melts at 54°C . (129.2°F .), boils at 173°C . (343.4°F .). Produced also by the action of PCl_5 on parachlorophenol.

Trichlorobenzenes, $\text{C}_6\text{H}_3\text{Cl}_3$.—The *unsymmetrical* modification 1 : 2 : 4, obtained by chlorination of benzene, by the action of PCl_5 on dichlorophenol, and from benzene hexachloride, $\text{C}_6\text{H}_6\text{Cl}_6$, by alcoholic potash, which removes 3HCl , forms colorless crystals, melts at 17°C . (62.6°F .), boils at 213°C . (415.4°F .).

The *symmetrical* modification 1 : 3 : 5 (or 2 : 4 : 6), obtained from trichloraniline, $\text{C}_6\text{H}_3\text{NH}_2\text{Cl.H.Cl.H}_3$, by exchange of NH_2 for H , or from dichloraniline, $\text{C}_6\text{H}_4\text{NH}_2\text{H.Cl.H}_3$, by exchange of NH_2 for Cl , melts at 63.4°C . (146.1°F .), boils at 208°C . (406.4°F .), sublimes at ordinary temperatures.

The *consecutive* modification 1 : 2 : 3, from trichloraniline $\text{C}_6\text{H}_3\text{NH}_2\text{Cl.Cl}$.

Cl_2H_2 , crystallizes from alcohol in large plates, melts at $532\text{--}540^\circ\text{C}$. ($127.40\text{--}129.20^\circ\text{F}$.), and boils at $2180\text{--}2190^\circ\text{C}$. ($4240\text{--}426.20^\circ\text{F}$.).

Tetrachlorobenzenes, $\text{C}_6\text{H}_2\text{Cl}_4$.—*Unsymmetrical* (1:3:4:5 or 1:2:4:6), from trichloraniline, $\text{C}_6\text{NH}_2\text{Cl}_3\text{H}$, forms colorless needles, melts at $500\text{--}510^\circ\text{C}$. ($1220\text{--}123.80^\circ\text{F}$.), boils at 2460°C . (474.80°F .). —*Symmetrical* (1:2:4:5), from benzene with chlorine, and from trichloraniline, $\text{C}_6\text{NH}_2\text{Cl}_3\text{H}$, forms slender needles, melts at $1370\text{--}1380^\circ\text{C}$. ($278.60\text{--}280.20^\circ\text{F}$.), boils at $2430\text{--}2460^\circ\text{C}$. ($469.40\text{--}474.80^\circ\text{F}$.). —*Unsymmetrical* (1:2:3:4), from trichloraniline, $\text{C}_6\text{NH}_2\text{Cl}_3\text{H}$, crystallizes in needles, melts at $450\text{--}460^\circ\text{C}$. ($1130\text{--}114.80^\circ\text{F}$.), boils at 2540°C . (489.20°F .).

Pentachlorobenzene, C_6HCl_5 , from benzene with chlorine, melts at 850°C . (1850°F .), boils at 2700°C . (5180°F .).

Hexachlorobenzene, C_6Cl_6 (Julin's chloride of carbon), is formed by chlorination of benzene in presence of iodine, SiCl_4 , or MoCl_5 , also by passing the vapor of chloroform or carbon dichloride, C_2Cl_4 , through a red-hot tube. Long, thin, colorless prisms; m. p. $2220\text{--}2230^\circ\text{C}$. ($431.60\text{--}438.80^\circ\text{F}$.); b. p. 3320°C . (629.60°F .).

Bromobenzenes.—**Monobromobenzenes**, $\text{C}_6\text{H}_5\text{Br}$, from benzene and bromine, and from phenol with PBr_3 , is a liquid boiling at 1560°C . (309.20°F .), and having a density of 1.519 at 00° .

Dibromobenzenes, $\text{C}_6\text{H}_4\text{Br}_2$.—Direct bromination of benzene (with aid of heat) yields chiefly the *para*-, with only a small quantity of the *ortho*-modification.

Para- (1:4).—Obtained from benzene, parabromophenol, and parabromaniline, melts at 890°C . (192.20°F .), boils at 2180°C . (424.40°F .), and yields a mononitro-derivative melting at 850°C . (1850°F .).

Meta- (1:3).—From metabromaniline, $\text{C}_6\text{NH}_2\text{H.Br.H}_2$, by exchange of NH_2 for Br, and from dibromaniline, $\text{C}_6\text{NH}_2\text{Br.H.Br.H}_2$, by exchange of NH_2 for H, is a liquid, boiling at 2190°C . (426.20°F .), of specific gravity 1.955 at 18.60°C . (65.50°F .), not solidifying at -200°C . (-320°F .); yields two mononitro-derivatives, $\text{C}_6\text{H}_4(\text{NO}_2)\text{Br}$, one melting at 610°C . (141.8°F .), the other at 82.50°C . (180.50°F .).

Ortho- (1:2), from orthobromaniline, and in small quantity from benzene and bromine. Liquid, solidifying below zero; m. p. -10°C . (130.2°F .); b. p. 223.80°C . (434.80°F .); sp. gr. 2.003 at 00° .

Tribromobenzenes, $\text{C}_6\text{H}_3\text{Br}_3$.—The *unsymmetrical* modification 1:2:4 or 1:3:4, is formed by the action of bromine on benzene, and from either of the three dibromobenzenes; hence its constitution is determined (p. 812); also from benzene hexbromide, $\text{C}_6\text{H}_6\text{Br}_6$, by the action of alcoholic potash, which abstracts 3HBr , and from dibromophenol, $\text{C}_6\text{OH.Br.H.Br.H}_2$, (exchange of OH for Br by the action of PBr_3), it melts at 440°C . (111.20°F .) and boils at 2750°C . (5270°F .). The *symmetrical* modification, 1:3:5, from tribromaniline $\text{C}_6\text{NH}_2\text{Br.H.Br.H.Br.H}_2$, melts at 119.50°C . (247.10°F .), and boils at about 2780°C . (532.4°F .). The *isomeric* modification, 1:2:3, from tribromaniline $\text{C}_6\text{NH}_2\text{H.Br.Br.Br.H}_2$, melts at 870°C . (188.60°F .).

Tetrabromobenzenes, $\text{C}_6\text{H}_2\text{Br}_4$.—*Unsymmetrical*, 1:3:4:5, from tribromophenol, $\text{C}_6\text{OH.H.Br.Br.Br.H}_2$, also from the corresponding tribromaniline, and from tetrabromaniline, forms colorless crystals, melting at 980°C . (208.40°F .). The *symmetrical* modification 1:2:4:5, from benzene with bromine, forms colorless needles melting at $1370\text{--}1400^\circ\text{C}$. ($2750\text{--}284^\circ\text{F}$.).

Pentabromobenzene, C_6HBr_5 , obtained by the bromination of benzene, forms colorless needles, subliming without decomposition, melting at about $240^\circ C.$ ($464^\circ F.$).

Hexabromobenzene, C_6Br_6 , is formed by the action of bromine on benzene in sunshine, or by heating benzene with bromine containing iodine; also from tetrabromomethane, CBr_4 , in small quantity by distillation, in larger quantity by heating to $300^\circ\text{--}400^\circ C.$ ($572^\circ\text{--}752^\circ F.$) in a sealed tube. Resembles hexachlorobenzene; melts at a temperature above $300^\circ C.$ ($572^\circ F.$).

It will be seen from the above that all the bromobenzenes are known except consecutive tetrabromobenzene.

Iodobenzenes are obtained by heating benzene with iodine and leucic acid to $200^\circ\text{--}240^\circ C.$ ($392^\circ\text{--}464^\circ F.$); by the action of iodine and phosphorus on phenol: by treating silver benzoate with iodine chloride; and from aniline and the iodonilines, similarly to the chlorine compounds.

C_6H_5I is a colorless liquid, boiling at $185^\circ C.$ ($365^\circ F.$): specific gravity 1.69.

$C_6H_4I_2$.—*Para*. Laminae; m. p. $127^\circ C.$ ($260.6^\circ F.$), b. p. $277^\circ C.$ ($530.6^\circ F.$).—*Meta*. Large shining laminae resembling naphthalene; m. p. $40.4^\circ C.$ ($104.7^\circ F.$); b. p. $284.7^\circ C.$ ($544.5^\circ F.$).

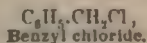
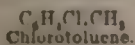
$C_6H_3I_3$. Needles melting at $76^\circ C.$ ($168.8^\circ F.$), and volatilizing without decomposition.

Fluobenzene, C_6H_5F , obtained by heating calcium fluobenzoate with slaked lime, is a scaly crystalline mass, melting at $40^\circ C.$ ($104^\circ F.$); boils at $180^\circ\text{--}183^\circ C.$ ($356^\circ\text{--}361.4^\circ F.$).

Toluene derivatives.

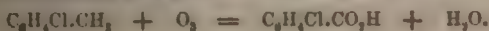
These compounds, as already observed, exhibit metameric modifications, according as the replacement of hydrogen atoms takes place in the principal or the lateral chain; and isomeric modifications determined by the orientation of the substituted radicles in the benzene-ring or principal chain (p. 813).

Chlorotoluenes.—Of monochlorinated toluenes there are two metameric modifications, viz.:—



the first produced by the action of chlorine on toluene at ordinary temperatures or in presence of iodine; the second by the action of chlorine on boiling toluene.

Chlorotoluene or **Tolyl Chloride**, $C_6H_4\begin{smallmatrix} CH_3 \\ | \\ Cl \end{smallmatrix}$, admits of three isomeric modifications, according to the relative positions of the chlorine and the methyl-group.—*Para*chlorotoluene, $C_6H_4(CH_3).H.H.Cl.H_2$, the chief product formed by the action of chlorine on toluene at ordinary temperatures, is a liquid solidifying at 0° , melting at $6.5^\circ C.$ ($43.7^\circ F.$), and boiling at $160^\circ C.$ ($320^\circ F.$). By oxidation with nitric acid, or with chromic acid mixture, it is converted into *para*chlorobenzoic acid:

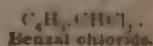
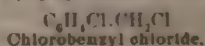
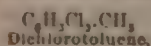


*Ortho*chlorotoluene, $C_6H_3Cl.CH_3$, produced in small quantity, together with the *para*-compound, is a liquid, boiling at $156^\circ C.$ ($312.8^\circ F.$), and

completely decomposed by chromic acid, without formation of a chlorobenzoic acid.—*Metachlorotoluene*, $C_6H_4H.Cl.Cl.H_3$, is prepared from *metaparatoluidine*, $C_6H_3H.Cl.NH_2.H_3$, by exchange of NH_2 for H , and converted by oxidation into *metachlorobenzoic acid*.

Benzyl chloride, $C_6H_5.CH_2Cl$, obtained by the action of chlorine on boiling toluene, and of PCl_3 on benzyl alcohol, $C_6H_5.CH_2OH$, is a liquid which gives off tear-exciting vapors, and boils at $176^\circ C.$ ($348.8^\circ F.$). It easily exchanges its chlorine-atom by double decomposition, being converted into acetate, cyanide, etc., by treatment with the corresponding potassium salts. It yields benzoic acid by oxidation, and is converted by heating with water and lead nitrate into benzaldehyde (bitter almond oil).

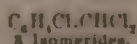
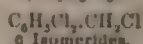
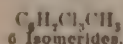
Of *dichlorotoluene*, $C_7H_6Cl_2$, there are three metamers, viz.



The first admits of six isomeric modifications, but only one is known, viz.

$C_6H_3H.Cl.Cl.Cl.H_3$, which is a liquid, boiling at $199^\circ C.$ ($384.9^\circ F.$), formed by chlorination of toluene.—*Chlorobenzyl chloride* admits of three isomerides, one of which is a liquid boiling at $213^\circ-214^\circ C.$ ($415.4^\circ-417.2^\circ F.$).—*Benzal chloride* (also called *chlorobenzal*) is formed by the action of chlorine on boiling toluene, and from benzaldehyde (bitter almond oil), by PCl_5 . Liquid having a pungent odor; sp. gr. 1.205 at $16^\circ C.$ ($60.8^\circ F.$); boils at $206^\circ C.$ ($402.8^\circ F.$); converted into benzaldehyde by heating with water to $20^\circ C.$ ($68^\circ F.$).

Trichlorotoluenes, $C_7H_5Cl_3$:

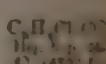
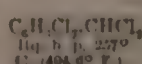
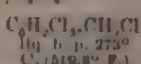
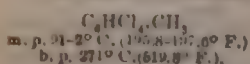


Trichlorotoluene, $C_6H_3Cl_3.CH_3$, obtained by chlorination of toluene, forms colorless crystals, melts at $76^\circ C.$ ($168.8^\circ F.$), boils at $235^\circ C.$ ($455^\circ F.$).

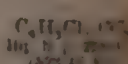
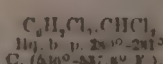
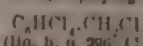
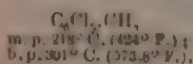
—*Dichlorobenzyl chloride*, $C_6H_4(CH_2Cl).H.Cl.Cl.H_3$, is a liquid boiling at $240^\circ C.$ ($465.8^\circ F.$).—*Chlorobenzal chloride (para)*, $C_6H_4(CHCl_2).H.H.Cl.H_3$, boils at $234^\circ C.$ ($453.2^\circ F.$).—*Benzotrichloride*, $C_6H_5.Cl_3$, formed by heating benzoyl chloride, $C_6H_5.COCl$, with PCl_5 , boils at $213^\circ-214^\circ C.$ ($415.4^\circ-417.2^\circ F.$).

Of the higher chlorotoluenes, some are liquid, some solid, at ordinary temperatures. The melting and boiling points of the known modifications are given in the following table:

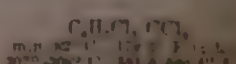
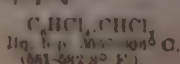
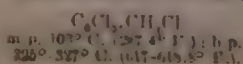
Tetrachlorotoluene, $C_7H_4Cl_4$:



Pentachlorotoluenes, $C_7H_3Cl_5$:



Hexachlorotoluenes, $C_7H_2Cl_6$:



heptachlorotoluenes, C_7HCl_7 :

$C_6Cl_5.CHCl_2$
m. p. $109^\circ C.$ ($228.2^\circ F.$); b. p.
 $334^\circ C.$ ($633.2^\circ F.$).

$C_6HCl_4.CCl_3$
m. p. $104^\circ C.$ ($210.2^\circ F.$); b. p.
 $316^\circ C.$ ($600.8^\circ F.$).

When an attempt is made to replace the last hydrogen-atom in toluene by chlorine, the molecule splits up, and perchlorobenzene is produced.

Bromotoluenes.—*Mono-*, $C_7H_7Br = C_6H_4Br.CH_3$.—The *ortho*- and *para*-modifications are formed by the action of bromine on toluidine; all the three modifications from the corresponding amidotoluenes (toluides) by heating the diazoperbromides with alcohol (see DIAZO-COMPOUNDS).

Ortho- Colorless liquid: sp. gr. 1.401 at $18^\circ C.$ ($64.4^\circ F.$); b. p. $182^\circ-183^\circ C.$ ($359.6^\circ-361.4^\circ F.$).

Meta- Colorless liquid; sp. gr. 1.4009 at $21^\circ C.$ ($69.8^\circ F.$); b. p. $184^\circ C.$ ($363.2^\circ F.$).

Para- Colorless crystals; m. p. $28.5^\circ C.$ ($83.3^\circ F.$); b. p. $185^\circ C.$ ($365^\circ F.$).

Benzyl bromide, $C_6H_5.CH_2Br$, obtained by bromination of toluene at the red heat, and by the action of hydrobromic acid on benzyl alcohol, is a liquid which gives off a tear-exciting vapor, has a sp. gr. of 1.438 at $0^\circ C.$ ($71.6^\circ F.$), and boils at $201^\circ C.$ ($393.6^\circ F.$).

Tetrabromotoluene, $C_6H_2Br_4.CH_3$, admits of six isomeric modifications, of which are known. $C_6H_2Br_3.Br.H.Br.H_2$ (1 : 2 : 4), obtained by direct bromination of toluene, crystallizes in needles; melts at $107^\circ-108^\circ C.$ ($224.6^\circ-226.4^\circ F.$); boils at $245^\circ C.$ ($473^\circ F.$). $C_6H_2Br_2.H.Br.Br.H_2$ (1 : 2), formed by the action of bromine in presence of iodine, and in sunlight, is a liquid boiling at $240^\circ C.$ ($464^\circ F.$). The other four modifications, whose boiling points lie between 237° and $246^\circ C.$ ($458.6^\circ-474.8^\circ F.$), are one liquid and two solid (m. p. 42.5° and $60^\circ C.$ ($108.5^\circ-140^\circ F.$)), are obtained from bromotoluidines, through the medium of the diazo-compounds.

Benzal bromide, $C_6H_5.CHBr_2$, formed by treating bitter almond oil with bromine, is a liquid which decomposes when distilled.

Iodotoluenes. $C_6H_4I.CH_3$.—The *ortho*- and *meta*-modifications are colorless liquids, the former boiling at $205^\circ C.$ ($401^\circ F.$), the latter at $207^\circ C.$ ($404.6^\circ F.$). *Para-iodotoluene* crystallizes in shining needles; melts at $35^\circ C.$ ($95^\circ F.$); boils at $211^\circ C.$ ($411.8^\circ F.$). All three are obtained by oxidation the corresponding iodobenzoic acids.

Benzyl iodide, $C_6H_5.CH_2I$, formed from the chloride by the action of hydriodic acid, melts at $24^\circ C.$ ($75.2^\circ F.$), and decomposes when sublimed.

Derivatives of the Hydrocarbons, C_8H_{10} .

Ethylbromobenzene, $C_6H_4Br.C_2H_5$, formed by the action of bromine on ethylbenzene at ordinary temperatures, is a colorless liquid, boiling at $190^\circ C.$ ($374^\circ F.$).—*Bromethylbenzene*, $C_6H_5.CHBr.CH_3$ (or $C_6H_5.CH_2.Br$), and the corresponding chloride, formed by the action of bromine or chlorine with aid of heat, are liquids which decompose when distilled.

The chloride, boiled with potassium cyanide and alcohol, is converted into the corresponding cyanide, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CN$, a colorless liquid, boiling at $261^\circ C.$ ($501.8^\circ F.$), having a sp. gr. of 1.0014 at $18^\circ C.$ ($64.4^\circ F.$), and forming the chief constituent of oil of water-cress.

Metaxylyl Chloride, $C_6H_4 \begin{smallmatrix} \text{CH}_3 \\ \diagup \\ \text{CH}_2\text{Cl} \end{smallmatrix}$, obtained by the action of chlorine on boiling metaxylene, is a colorless liquid, boiling at $195^\circ C.$ ($383^\circ F.$).

Monobromometaxylene, $C_6H_4 \cdot Br \cdot CH_2 \cdot H \cdot CH_2 \cdot H_2$, from metaxylene and bromine, boils at $204^\circ\text{--}205^\circ C.$ ($399.2^\circ\text{--}401^\circ F.$).—An isomeric compound (1 : 3 : 5), formed by the action of nitrous acid and alcohol on bromometaxyline, is a liquid boiling at $204^\circ C.$ ($399.2^\circ F.$), not solidifying at $20^\circ C.$ ($68^\circ F.$), and having a sp. gr. of 1.362 at 20° .

Dibromometaxylene, $C_6H_4Br_2(CH_3)_2$, from metaxylene and bromine, forms colorless shining crystalline scales, m. p. $72^\circ C.$ ($161.6^\circ F.$), b. p. $256^\circ C.$ ($492.8^\circ F.$). **Tetrabromometaxylene**, $C_6Br_4(CH_3)_2$, forms long slender needles, slightly soluble in alcohol, melting at $241^\circ C.$ ($465.8^\circ F.$).

Bromoparaxylene, $C_6H_4Br(CH_3)_2$, forms colorless shining tables, melts at $10^\circ C.$ ($50^\circ F.$); boils at $200^\circ C.$ ($392^\circ F.$). **Dibromoparaxylene** melts at $72^\circ C.$ ($161.6^\circ F.$), and resembles the meta-compounds in all other respects.

Tollylene chloride, $C_6H_4(CH_2Cl)_2$, and **Tollylene bromide**, $C_6H_4(CH_2Br)_2$, formed by the action of chlorine or bromine on boiling paraxylene, crystallizes in colorless laminae. The chloride melts at 100° , and boils, with partial decomposition, at $240^\circ\text{--}250^\circ C.$ ($464^\circ\text{--}482^\circ F.$); the bromide melts at $145^\circ\text{--}147^\circ C.$ ($293^\circ\text{--}296.6^\circ F.$). Both compounds, when treated with potassium cyanide in alcoholic solution, yield tollylene cyanide, $C_6H_4(CH_2CN)_2$.

CYANOGEN-DERIVATIVES.

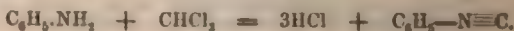
Cyanobenzene, $C_6H_5 \cdot CN$ (*Benzonitril*, *Phenyl Cyanide*), is formed, like the nitrils of the fatty group (p. 537), by dehydration of ammonium benzoate, $C_6H_5O_2 \cdot NH_4$, and by distilling the potassium salt of benzenesulphonic acid with potassium cyanide (or the dry ferrocyanide):



also by heating phenyl isocyanide with metallic copper, and by other reactions. It is an oily liquid, smelling like bitter almond oil, having a density of 1.023 at 0° , and boiling at $191^\circ C.$ ($375.8^\circ F.$). It unites with the halogen-elements, the haloid acids, and hydrogen.

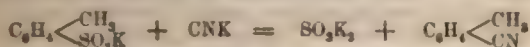
Substituted benzonitrils are obtained by dehydration of substituted benzamides, e. g., $C_6H_4Br \cdot CN$, by the action of phosphoric anhydride on bromobenzamide, $C_6H_4Br \cdot CONH_2$.

Phenyl Isocyanide or **Phenyl-carbamine**, $C \equiv N - C_6H_5$, isomeric with benzonitril, is formed by distilling aniline with chloroform and alcoholic potash:



a liquid having a strong smell of prussic acid, and boiling, with decomposition, at 167°C . (332.6°F). It is dichroic; blue by reflected, green by transmitted light. It is not altered by alkalis, but acids convert it into aniline and formic acid. Heated to 200°C . (392°F .) it changes to benzonitril.

Cyanotoluene, $\text{C}_6\text{H}_4(\text{CN})\cdot\text{CH}_3$. *Tolunitril*.—The three isomeric modifications of this compound are formed by treating the respective tolyl-sulphurimides, $\text{N} \left\{ \begin{array}{l} \text{C}^{\text{S}} \\ \text{C}_6\text{H}_4\cdot\text{CH}_3 \end{array} \right.$, with finely divided copper, which removes sulphur, or by distilling the potassium salts of the corresponding toluenesulphonic acids with potassium cyanide:

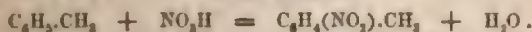


Para.—Colorless liquid, smelling like nitrobenzene, boiling at $203^{\circ}\text{--}204^{\circ}\text{C}$. ($397.6^{\circ}\text{--}399.2^{\circ}\text{F}$). *Pure*.—Colorless needles, melting at 28.5°C . (83°F); boiling at 218°C . (424°F). *Meta*.—Not yet obtained in the pure state.

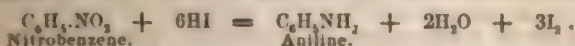
Benzyl Cyanide, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CN}$, constitutes the principal part of the volatile oils of the garden nasturtium (*Tropaeolum majus*), and of the garden cress (*Lepidium sativum*), and is produced artificially by heating benzyl chloride with alcohol and potassium cyanide. Colorless liquid boiling at 100°C . (442.6°F); specific gravity 1.0146 at 18°C . (64.4°F).

NITRO-DERIVATIVES.

These bodies are easily formed by the action of concentrated or fuming nitric acid on benzene and its homologues, the substitution of the NO_2 -group for hydrogen taking place in the benzene-nucleus, never in the radical chains; e. g.,



On pouring the product into water, the nitro-compound separates out, usually in the form of a thick yellow or orange-colored oil. The more highly nitrated derivatives are most easily obtained by the action of a mixture of 1 part of strong nitric acid and 2 parts of strong sulphuric acid. The aromatic nitro-compounds are mostly of a yellow color; a few are solid, the rest crystalline solids. By hydrogen sulphide or ammonium hydride, and by stannous chloride, they are reduced to amide-compounds; sodium-amalgam, or by heating with alcoholic potash, to azo-compounds. They may also be converted into amide-compounds by heating with hydriodic acid:



Nitrobenzenes.—Mononitrobenzene, $\text{C}_6\text{H}_5(\text{NO}_2)$, formed by gradually adding benzene to strong nitric acid in a cooled vessel, is a light yellow liquid, having an aromatic odor, boiling at 220°C . (428°F), melting at $+3^{\circ}\text{C}$. (37.4°F). Sp. gr. 1.20 at 0° .

Di-nitrobenzenes, $\text{C}_6\text{H}_4(\text{NO}_2)_2$.—The three modifications are formed either by dropping benzene into a mixture of 2 vols. strong sulphuric

and 1 vol. very strong nitric acid; and on crystallizing the product from alcohol, the meta-compound, which constitutes by far the largest portion, separates out, while the other two remain in solution.

The *ortho*-compound, which forms the smallest portion of the product, crystallizes from hot water in long needles, melting at 118° C. (244° F.), soluble in 26 parts of alcohol at 24° C. (75.2° F.), and in 3 parts of boiling alcohol.

The *meta*-compound (ordinary dinitrobenzene), forms long rhombic prisms melting at 89.8° C. (194.2° F.), soluble in 17 parts of alcohol at 24° C. (75.2° F.), and in all proportions of boiling alcohol.

The *para*-compound forms fan-shaped groups of monoclinic prisms, melting at 171° – 172° C. (339.8° – 347.6° F.), sparingly soluble in alcohol.

Trinitrobenzene, $C_6H_3(NO_2)_3$, formed by heating metadinitrobenzene with a mixture of pyrosulphuric acid (p. 197) and very strong nitric acid in sealed tubes, to 130° – 140° C. (266° – 284° F.), crystallizes from alcohol in white laminae or fern-like groups of needles. It melts at 124° – 125° C. (249.8° – 251.0° F.), dissolves sparingly in cold alcohol, easily in hot alcohol and ether.

Nitro-haloid Derivatives of Benzene.—The action of nitric acid or a mixture of nitric and sulphuric acids, on the chloro-, bromo-, and iodo-benzenes, gives rise to *para*- and *ortho*-mononitro-derivatives of the haloid compounds, the former being always produced in greatest abundance. The same products are obtained from the corresponding nitranilines, $C_6H_4NO_2.NH_2$, by exchange of the NH_2 for Cl, Br, or I, through the medium of the diazo-compounds. The *meta*-compounds are obtained in like manner from metanitraniline; metanitrochlorobenzene also by passing chlorine into nitrobenzene mixed with iodine, or, better, with $SbCl_3$.

The following are the melting and boiling points of the isomeric mononitro-, chloro-, bromo-, and iodo-benzenes, $C_6H_4X(NO_2)$:

| | Melting Points. | | |
|------------------|---|---|--|
| | (1 : 3) | (1 : 3) | (1 : 4) |
| $C_6H_4Cl(NO_2)$ | 32.5° C. (90.5° F.) | 44.4° C. (111.9° F.) | 88° C. (191.4° F.) |
| $C_6H_4Br(NO_2)$ | 41.5° C. (106.7° F.) | 56° C. (132.8° F.) | 126° C. (258.8° F.) |
| $C_6H_4I(NO_2)$ | 49.4° C. (120.9° F.) | 30° C. (86.8° F.) | 171° C. (339.8° F.) |

| | Boiling Points. | | |
|------------------|--|--|--|
| | (1 : 3) | (1 : 3) | (1 : 4) |
| $C_6H_4Cl(NO_2)$ | 243° C. (469.4° F.) | 233° C. (451.4° F.) | 242° C. (467.6° F.) |
| $C_6H_4Br(NO_2)$ | 261° C. (501.8° F.) | 256.5° C. (493.7° F.) | 255° C. (491° F.) |
| $C_6H_4I(NO_2)$ | ... | 280° C. (536° F.) | ... |

These numbers show that the *para*-derivatives have the highest melting points, and the *ortho*-derivatives for the most part the lowest; the relations between the boiling points are less regular. The *ortho*- and *para*-compounds, heated in sealed tubes with aqueous potash, are converted into the corresponding phenols, $C_6H_4Cl.OH$, etc., whereas the *meta*-compounds do not exhibit this transformation.

Nitrodichloro- and Nitrodibromobenzenes, $C_6H_2Cl_2(NO_2)$, and $C_6H_2Br_2(NO_2)$.—These compounds are all crystalline, and melt at the temperatures shown in the following table.—

| $C_6H_4Cl_2(NO_2)$ | $C_6H_3Br_2(NO_2)$ |
|---------------------------------------|---------------------------------------|
| 1 : 2 : 4* . . . 32.2° C. (90.0° F.) | 1 : 2 : 4 . . . 61.6° C. (142.9° F.) |
| 1 : 2 : 5 . . . 55.0° C. (131.0° F.) | 1 : 2 : 5 . . . 85.4° C. (185.7° F.) |
| 1 : 3 : 5 . . . 65.4° C. (149.7° F.) | 1 : 3 : 5 . . . 104.5° C. (220.1° F.) |
| 1 : 3 : 4 . . . 43.0° C. (109.4° F.) | 1 : 3 : 4 . . . 58.6° C. (137.5° F.) |
| | 1 : 2 : 6 . . . 82.6° C. (180.7° F.) |

Dinitrochlorobenzene, $C_6H_4Cl(NO_2)_2$, formed by treating either (1 : 2) or (1 : 4) chlorobenzene with a mixture of nitric and sulphuric acids, and from the corresponding dinitrophenol, $C_6H_3(NO_2)_2.OH$, by the action of PCl_5 , crystallizes in prisms melting at 53.4° C. (128.1° F.). $C_6H_3Cl(NO_2)_2$, formed in like manner from (1 : 3) nitrochlorobenzene, exhibits dimorphous modifications having different melting points—36.3°–38.8° C. (97.3°–101.8° F.).

Dinitrobromobenzene, $C_6H_3Br(NO_2)_2$, is known in two modifications analogous to the chlorine-compounds just described, and obtained in like manner. Both are crystalline; (1 : 2 : 4) melts at 75.3° C. (167.5° F.); (1 : 3 : 4) at 59.4° C. (138.9° F.).

Dinitroiodobenzene, $C_6H_2I(NO_2)_2$, from para- and ortho-iodobenzene with nitrosulphuric acid, forms large yellow, transparent plates or prisms, melting at 88.5° C. (190.9° F.).

Another modification, $C_6H_2I_2(NO_2)_2$, formed simultaneously with the last, crystallizes in transparent orange-colored rhombic tables, melting at 113.7° C. (236.7° F.).

Trinitrochlorobenzene, $C_6Cl(NO_2)_3$, (*Picryl chloride*), from picric acid, $C_6H_2(NO_2)_3.OH$, with PCl_5 , forms needles melting at 83° C. (181.4° F.), and, like picric acid, forms crystalline compounds with many hydrocarbons.

Nitrotoluenes.—*Para-* and *orthonitrotoluene*, $C_6H_4(NO_2).CH_3$, are formed by treating toluene with fuming nitric acid, and may be separated by fractional distillation. The former crystallizes in nearly colorless prisms, melts at 54° C. (129.2° F.), and boils at 236° C. (456.8° F.). The latter is a yellowish liquid boiling at 222°–223° C. (437.6°–433.4° F.).

Metanitrotoluene, obtained by the action of nitrous acid and alcohol on metanitroparatoluidine, $C_6H_4.NH_2.NO_2$, is crystalline, melts at 16° C. (60.8° F.), and boils at 230°–231° C. (446°–447.8° F.).

Diinitrotoluene, $C_6H_3(NO_2)_2$, formed by treating toluene, or ortho- or para-nitrotoluene with nitro-sulphuric acid, crystallizes in long colorless needles, melting at 70.5° C. (159.7° F.). Another modification, obtained in like manner from metanitrotoluene, melts at 60° C. (140° F.).

Trinitrotoluene, $C_6H_2(NO_2)_3$, obtained by prolonged heating of a solution of toluene in nitrosulphuric acid, forms nearly colorless needles, slightly soluble in alcohol, melting at 82° C. (179.6° F.).

Nitro-ethyl-benzenes, $C_6H_4(NO_2).C_2H_5$ (*ortho-* and *para-*), are formed simultaneously by the action of fuming nitric acid on ethyl-benzene. Both are liquid, the former boiling at 227°–228° C. (440.6°–442.4° F.), the latter at 245°–246° C. (473°–474.8° F.). With tin and hydrochloric acid, they yield liquid bases, one of which, viz., *paramido-ethylbenzene*, $C_6H_4(NH_2).C_2H_5$, is also produced by heating the hydrochloride of ethylaniline to 300°–330° C. (572°–626° F.).

* NO_2 in the position 1, in all the formulae.

Nitroparaxylene, $C_8H_7(NO_2)(CH_3)_2$, is a pale yellow liquid which boils at 234° – 237° C. (453.2° – 458.6° F.), and does not solidify in a freezing mixture.—**Dinitroparaxylene**, $C_8H_7(NO_2)_2(CH_3)_2$. Two isomeric forms of this compound are formed simultaneously by the action of fuming nitric acid on paraxylene, the less soluble in alcohol of the two forming long thin needles melting at 123.5° C. (254.3° F.), while the other, which is more soluble in alcohol, forms large monoclinic crystals melting at 7° C. (199.4° F.).

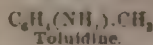
Trinitroparaxylene, $C_8H(NO_2)_3(CH_3)_2$, forms long, colorless needles, melting at 137° C. (278.6° F.), moderately soluble in hot, sparingly in cold alcohol.

Nitromesitylene, $C_9H_7(NO_2)(CH_3)_3$, forms nearly colorless prisms easily soluble in alcohol, melts at 42° C. (107.6° F.), boils at 254° C. (481° F.).—**Dinitromesitylene**, $C_9H(NO_2)_2(CH_3)_3$. Slender, colorless, brilliant needles, melting at 86° C. (186.8° F.).—**Trinitromesitylene**, $C_9H(NO_2)_3(CH_3)_3$. Needles very slightly soluble in alcohol, melting at 232° C. (449.6° F.).

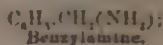
Nitropseudocumene, $C_9H_{11}(NO_2)$, forms long needles, easily soluble in hot alcohol, melts at 71° C. (159.8° F.), boils at 265° C. (509° F.).—**Trinitropseudocumene**, $C_9H_5(NO_2)_3$. Colorless, quadratic prisms, melting at 185° C. (365° F.).

AMIDO-DERIVATIVES.

The replacement of hydrogen by NH_2 in the hydrocarbons homologous with benzene, gives rise to two series of metameric compounds, analogous to the haloid and nitro-derivatives above described; thus, from toluene, $C_6H_5.CH_3$, are derived:

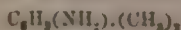


Toluidine.

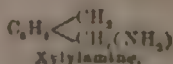


Benzylamine.

and from xylene, $C_8H_7(CH_3)_2$:



Xyloidine.

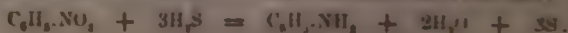


Xylylamine.

These compounds are all of basic character; but those in which the NH_2 is situated in the lateral chains are stronger bases than their metamers containing this group in the principal chain, and are analogous in these properties and their mode of formation to the amines of the fatty group; thus benzylamine, which may be represented by the formula $NH_2.C_6H_5$, derived from ammonia by substitution of benzyl, C_6H_5 , for hydrogen, is formed, together with ditenzylamine, $NH(C_6H_5)_2$, and tribenzylamine, $N(C_6H_5)_3$, by heating benzyl chloride with ammonia, just as ethylamine is formed from the chloride, bromide, or iodide of ethyl. Toluidine and its homologues, on the other hand, are produced chiefly by the action of reducing agents on the nitro-derivatives; and amidobenzene, aniline, or phenylamine, $C_6H_5-NH_2$, which may be regarded as the first term of either series, is formed for the most part in the same manner.

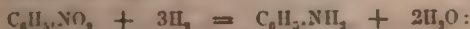
The reduction of the nitro-derivatives is effected:

1. By the action of ammonium sulphide in alcoholic solution:

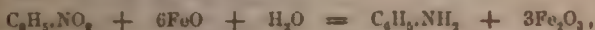


the application of this method to di- and tri-nitro-compounds, only one nitro-group is reduced in the first instance, so that nitro-amido compounds are obtained, such as $C_6H_5 \begin{smallmatrix} NO_2 \\ \diagdown \\ NH_2 \end{smallmatrix}$.

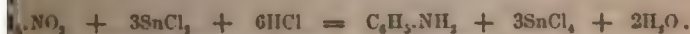
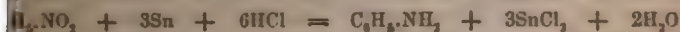
By the action of zinc or tin and hydrochloric acid, or of iron filings and acetic acid. In these cases, the reduction may be supposed to be effected by nascent hydrogen:



the case of iron and acetic acid, also through the intervention of the ferrous salt formed in the first instance:



In that of tin and hydrochloric acid, through the intervention of stannous chloride:



To effect this last reaction, the nitro-compound is drenched with fuming hydrochloric acid, and the calculated quantity of granulated tin is gradually added. The action usually begins after a while, without application of heat, the tin and the nitro-compound dissolving. From the warm solution, which contains a double salt, consisting of the hydrochloride of the aniline base combined with stannic chloride, *e. g.* $(C_6H_5NH_2.HCl)_2.SnCl_4$, tin is precipitated by hydrogen sulphide, and the stannic sulphide is separated by filtration, leaving the hydrochloride of the amido-compound in solution.

When a di- or a tri-nitro-compound is thus treated, all the nitro-groups are usually reduced at once: hence this process is especially applicable to the preparation of di- and tri-amido-derivatives. If, however, only half the calculated quantity of tin be added, a partial reduction may be effected, and nitro-amido-compounds obtained.

Amidobenzenes.

Aniline, $C_6H_5N = C_6H_5NH_2$.—*Phenylamine*.—This base, which is now prepared in enormous quantities for the manufacture of coloring matters, was discovered in 1826 by Unverdorben, who obtained it by the dry distillation of indigo. Fritzsche, in 1841, found that it might be obtained by heating indigo with potash-lye; and Zinin, about the same time, introduced the method of preparing it by reduction of nitrobenzene with ammonium sulphide—a process which, as already observed, is very generally applicable to the preparation of organic bases.

To prepare aniline in this way, an alcoholic solution of nitrobenzene is mixed with ammonia, and gaseous hydrogen sulphide is passed into the acid as long as sulphur continues to be precipitated: the reaction is greatly accelerated by warming the liquid. The solution is then mixed with excess of acid, filtered to separate the sulphur, boiled to expel alcohol and excess of nitrobenzene, and then distilled with excess of potash.

On the large scale, aniline is prepared by reducing nitrobenzene with iron and acetic acid. Nitrobenzene (1 part) is heated with iron filings ($1\frac{1}{2}$ part), glacial acetic acid (1 part), and the solid product of the reaction is

Nitroparaxylene, $C_8H_7(NO_2)(CH_3)_2$, is a pale yellow liquid which boils at $234.0-237.0^\circ C.$ ($453.2-458.6^\circ F.$), and does not solidify in a freezing mixture.—**Dinitroparaxylene**, $C_8H_5(NO_2)_2(CH_3)_2$. Two modifications of this compound are formed simultaneously by the action of fuming nitric acid on paraxylene, the less soluble in alcohol of the two forming long thin needles melting at $123.5^\circ C.$ ($254.3^\circ F.$), while the other, which is more soluble in alcohol, forms large monoclinic crystals melting at $204.1^\circ C.$ ($399.4^\circ F.$).

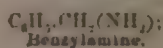
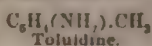
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Nitromesitylene, $C_9H_7(NO_2)(CH_3)_3$, forms nearly colorless prisms, easily soluble in alcohol, melts at $42^\circ C.$ ($107.6^\circ F.$), boils at $221^\circ C.$ ($431^\circ F.$).—**Dinitromesitylene**, $C_9H_5(NO_2)_2(CH_3)_3$. Slender, colorless, vertical needles, melting at $86^\circ C.$ ($186.8^\circ F.$).—**Trinitromesitylene**, $C_9H_3(NO_2)_3(CH_3)_3$. Needles very slightly soluble in alcohol, melting at $232^\circ C.$ ($449.6^\circ F.$).

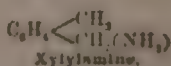
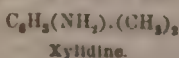
Nitropseudocumene, $C_9H_9(NO_2)$, forms long needles, easily soluble in hot alcohol, melts at $71^\circ C.$ ($159.8^\circ F.$), boils at $265^\circ C.$ ($509^\circ F.$).—**Trinitropseudocumene**, $C_9H_7(NO_2)_3$. Colorless, quadratic prisms, melting at $185^\circ C.$ (365°).

AMIDO-DERIVATIVES.

The replacement of hydrogen by NH_2 in the hydrocarbons homologous with benzene, gives rise to two series of metameric compounds, analogous to the haloid and nitro-derivatives above described: thus, from toluene, $C_6H_5.CH_3$, are derived:



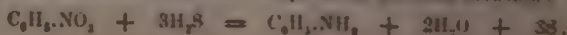
and from xylene, $C_6H_4(CH_3)_2$:



These compounds are all of basic character; but those in which the NH_2 is situated in the lateral chains are stronger bases than their metamers containing this group in the principal chain, and are analogous in their properties and their mode of formation to the amines of the fatty group; thus benzylamine, which may be represented by the formula $NH_2.C_6H_5$, is derived from ammonia by substitution of benzyl, C_6H_5 , for hydrogen; is formed, together with dibenzylamine, $NH(C_6H_5)_2$, and tribenzylamine, $N(C_6H_5)_3$, by heating benzyl chloride with ammonia, just as ethylamine is formed from the chloride, bromide, or iodide of ethyl. Toluidine and its homologues, on the other hand, are produced chiefly by the action of reducing agents on the nitro-derivatives; and amidobenzene, another member of the series, is formed for the most part in the same manner.

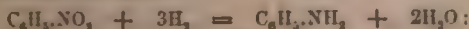
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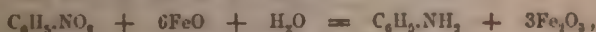


In the application of this method to di- and tri-nitro-compounds, only one nitro-group is reduced in the first instance, so that nitro-amido compounds are obtained, such as $C_6H_5 \begin{smallmatrix} NO_2 \\ \diagdown \\ NH_2 \end{smallmatrix}$.

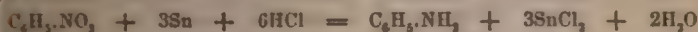
2. By the action of zinc or tin and hydrochloric acid, or of iron filings and acetic acid. In these cases, the reduction may be supposed to be effected by nascent hydrogen:



In the case of iron and acetic acid, also through the intervention of the ferrous salt formed in the first instance:



and in that of tin and hydrochloric acid, through the intervention of stannous chloride:



and



To effect this last reaction, the nitro-compound is drenched with fuming hydrochloric acid, and the calculated quantity of granulated tin is gradually added. The action usually begins after a while, without application of heat, the tin and the nitro-compound dissolving. From the warm solution, which contains a double salt, consisting of the hydrochloride of the resulting base combined with stannic chloride, *e. g.* $(C_6H_5.NH_2.HCl)_2.SnCl_4$, the tin is precipitated by hydrogen sulphide, and the stannic sulphide is separated by filtration, leaving the hydrochloride of the amido-compound in solution.

When a di- or a tri-nitro-compound is thus treated, all the nitro-groups are usually reduced at once: hence this process is especially applicable to the preparation of di- and tri-amido-derivatives. If, however, only half the calculated quantity of tin be added, a partial reduction may be effected, and nitro-amido-compounds obtained.

Amidobenzenes.

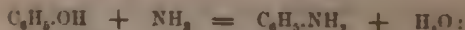
Aniline, $C_6H_5.N = C_6H_5.NH_2$.—*Phenylamine*.—This base, which is now prepared in enormous quantities for the manufacture of coloring matters, was discovered in 1826 by Unverdorben, who obtained it by the dry distillation of indigo. Fritzsche, in 1841, found that it might be obtained by heating indigo with potash-lye; and Zinin, about the same time, introduced the method of preparing it by reduction of nitrobenzene with ammonium sulphide—a process which, as already observed, is very generally applicable to the preparation of organic bases.

To prepare aniline in this way, an alcoholic solution of nitrobenzene is mixed with ammonia, and gaseous hydrogen sulphide is passed into the liquid as long as sulphur continues to be precipitated: the reaction is greatly accelerated by warming the liquid. The solution is then mixed with excess of acid, filtered to separate the sulphur, boiled to expel alcohol and excess of nitrobenzene, and then distilled with excess of potash.

On the large scale, aniline is prepared by reducing nitrobenzene with ferrous acetate. Nitrobenzene (1 part) is heated with iron filings ($1\frac{1}{2}$ part), and glacial acetic acid (1 part), and the solid product of the reaction is

mixed with lime, and distilled with superheated steam. On the small scale, the best results are obtained by reduction with tin and hydrochloric acid. The product obtained by either process may be purified by converting it into oxalate, crystallizing this salt several times from alcohol, and decomposing it with potash.

Aniline is also produced by heating phenol with ammonium chloride and fuming hydrochloric acid in sealed tubes to 315°C . (599°F .) for about thirty hours:



and lastly, it is formed by the destructive distillation of nitrogenous organic matters, and is one of the constituents of coal-tar oil.

Aniline is a colorless oily liquid, having a faint peculiar odor, a density of 1.036 at 0° , and boiling at 184.5°C . (364.1°F .). When quite pure it solidifies at low temperatures, and melts at -8°C . (17.6°F .). It dissolves but sparingly in water—31 parts at 12°C . (53.6°F .), easily in alcohol and ether. When exposed to the air it turns brown and gradually resinizes. Its aqueous solution, mixed with chloride of lime, assumes a purple-violet color. Its solution in strong sulphuric acid acquires, on addition of a few drops of aqueous potassium dichromate, first a red, then a deep-blue color. A deal shaving dipped in aniline is colored yellow.

Aniline is a strong base, uniting directly with acids and with certain salts, forming, for example, the compounds $(\text{C}_6\text{H}_5\text{N})_2\text{SnCl}_2$ and $(\text{C}_6\text{H}_5\text{N})_2\text{CuSO}_4$.—The *hydrochloride*, $\text{C}_6\text{H}_5\text{N.HCl}$, forms needles very soluble in water and in alcohol, subliming without decomposition. Its alcoholic solution, mixed with platinum chloride, deposits the *platinchloride*, $(\text{C}_6\text{H}_5\text{N.HCl})_2\text{PtCl}_6$, in yellow needles. The *nitrate*, $\text{C}_6\text{H}_5\text{N.NO}_3\text{H}$, crystallizes in large rhombic tables; the *oxalate*, $(\text{C}_6\text{H}_5\text{N})_2\text{C}_2\text{O}_4\text{H}_2$, separates from a mixture of the alcoholic solutions of aniline and oxalic acid, in rhombic prisms.

SUBSTITUTION-PRODUCTS OF ANILINE.

1. *Halogen-Derivatives*.—These compounds are formed:

(1) By the action of halogen-elements on aniline, bromine, and chlorine, forming di- or tri-derivatives, iodine giving rise to para-iodaniline. The monochlor- and monobromanilines (para) are obtained by the action of chlorine and bromine, in vapor or in aqueous solution, on acetanilide, $\text{C}_6\text{H}_5\text{NH}(\text{C}_2\text{H}_5\text{O})$, suspended in water.

(2) By reduction of the nitrochloro-, nitrobromo-, or nitroiodo-benzenes with ammonium sulphide, or with tin and hydrochloric acid, $\text{C}_6\text{H}_5\text{Cl}(\text{NO}_2)$, for example, being thus converted into $\text{C}_6\text{H}_5\text{Cl}(\text{NH}_2)$.

(3) From the nitranilines by substitution of Cl, Br, or I for NH_2 (through the medium of the diazo-compounds), and of NH_2 for NO_2 by the action of reducing agents, $\text{C}_6\text{H}_5\text{Cl} < \text{NH}_2$ for example from $\text{C}_6\text{H}_5\text{Cl} < \text{NO}_2$.

By the entrance of halogen-elements (also of the nitro-group) into the molecule, the basic properties of aniline are weakened. The monoderivatives are weak bases; the di-derivatives form, for the most part, very unstable salts which are decomposed even by water; and the tri-derivatives are mostly destitute of basic properties, though the orientation of the substituted radicals has some influence in this respect. In the monoderivatives, the ortho-compounds are less basic than the meta- and para-compounds.

The following table exhibits the modes of formation and the chief physical properties of the halogen-derivatives of aniline:

| | temperatures. | setting points. | melting point. |
|--|--|--|--|
| Chloranilines.
Mono- $C_6H_4Cl(NH_2)$
Ortho (1 : 2)
Meta (1 : 3)
Para (1 : 4)

Di- $C_6H_3Cl_2(NH_2)$
1 : 2 : 4*
1 : 2 : 5
1 : 3 : 5
1 : 3 : 4

Tri- $C_6H_2Cl_3(NH_2)$
1 : 2 : 4 : 5
1 : 2 : 4 : 6 | from 1 : 2 $C_6H_4Cl(NO_2)$
1 : 3 "
1 : 4 "

from dichloroacetanilide and di-
chloraniline by potash
from 1 : 2 : 5 $C_6H_3Cl_2(NO_2)$
" 1 : 3 : 5 "
" 1 : 3 : 4 " | —14° C. (6.8° F.)
70–71° C. (156–156.9° F.)

63° C. (145.4° F.)
50° C. (122° F.)
50.5° C. (122.9° F.)
71.5° C. (160.7° F.)

77.5° C. (171.5° F.)
96.5° C. (205.7° F.)

31.5° C. (88.7° F.)
18–18.8° C. (64.4–65.5° F.)
64° C. (147.2° F.) | 207° C. (404.6° F.)
250° C. (440° F.)
230–251° C.
(446–447.8° F.)

245° C. (473° F.)

272° C. (521.6° F.)

250° C. (500° F.)
270° C. (518° F.)

228° C. (444.2° F.)
251° C. (483.8° F.)
Decomposed by
distillation
into aniline,
1 : 2 : 4 di-, and
1 : 2 : 4 : 6 tri-
bromaniline. |
| Bromanilines.
Mono- $C_6H_4Br(NH_2)$
Ortho (1 : 2)
Meta (1 : 3)
Para (1 : 4) | from 1 : 2 $C_6H_4Br(NO_2)$
" 1 : 3 "
" 1 : 4 " | Colorless needles; insoluble in
water, very soluble in alcohol
Crystalline mass
Larger rhombic crystals, looking
like regular octahedrons | |

 * NH_2 in position 1 throughout.

| | Formation. | Physical character at ordinary temperatures. | Melting point. | Boiling point. |
|---|---|---|---|----------------|
| Bromanilines—con. | | | | |
| <i>Di.</i> $C_6H_3Br_2(NH_2)$
1 : 3 : 4 | from aniline with Br_2 from dibromacetanilide with alkalis; from 1 : 2 : 6 $C_6H_3Br_2(NO_2)$ by reduction; from $C_6H_4NO_2$ by heating with conc. HBr to 180°–190° (together with mono- and tribromaniline), and by distilling dibromaniline with potash
from 1 : 2 : 6 $C_6H_3Br_2(NO_2)$
" 1 : 3 : 6
" 1 : 3 : 4 | colorless shining needles. | 75.5° C. (175.1° F.) | |
| 1 : 2 : 6
1 : 3 : 6
1 : 3 : 4 | | Warty groups of silky prisms
white needles
(colorless needles; this and 1 : 3 : 6 are more basic than the two former) | 81–82° C. (133.8–135.0° F.)
80.4° C. (133.5° F.)
80.4° C. (175.7° F.) | |
| <i>Tri.</i> $C_6H_2Br_3(NH_2)$
1 : 2 : 4 : 6 | from aniline, para- and ortho-bromaniline, with excess of Br_2 , and by reduction of 1 : 2 : 6 $C_6H_3Br_2(NO_2)$
(from 1 : 3 : 4 : 6 $C_6H_3Br_2(NO_2)$) | Long colorless needles non-basic | 119.6° C. (247.3° F.) | |
| 1 : 3 : 4 : 6 | | | | |
| <i>Tetra.</i> $C_6HBr_4(NH_2)$
1 : 2 : 3 : 4 : 6 | from 1 : 3 bromaniline and 1 : 2 : 6 di-bromaniline with excess of bromine
from 1 : 3 : 6 di-bromaniline with Br_2 | Crystalline: unites with acids

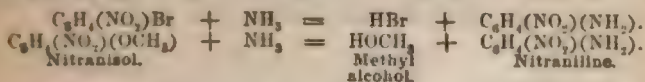
Fine long silky needles | Does not melt at 130° C. (266° F.)
113.5° C. (230.3° F.) | |
| <i>Penta.</i> $C_6Br_5(NH_2)$ | | Large needles | Does not melt at 250° C. (451.6° F.) | |
| Iodanilines. | | | | |
| <i>Meta.</i> $C_6H_4LI(NH_2)$ (1 : 3) | from 1 : 3 $C_6H_3I(NO_2)$ | Silvery laminae | 30° C. (71° F.) | |
| <i>Para.</i> " (1 : 4) | " 1 : 4 " | Colorless needles | 50° C. (122° F.) | |

2. Nitro-derivatives.

Mononitranilines, $C_6H_4(NO_2).NH_2$.—The three isomeric derivatives are formed by imperfect reduction of the dinitrobenzenes (p. 831), best by passing hydrogen sulphide into the alcoholic solution of the nitro compound, mixed with a little concentrated ammonia :



The ortho- and para-derivatives are also formed by the action of alkalis on the corresponding nitro-acetanilides, $C_6H_5.NH(C_2H_3O)$, and by prolonged heating of ortho- and para-nitrobromobenzene, or of the methylic ether of ortho- or paranitrophenol, with aqueous or alcoholic ammonia to $180-200^\circ C.$ ($356-392^\circ F.$).

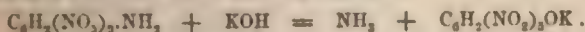


Ortho-nitraniline forms long, dark yellow needles, melting at $71.5^\circ C.$ ($160.7^\circ F.$), more soluble in water and in alcohol than the other two modifications. *Meta*.—Long yellow prisms, melting at $109^\circ C.$ ($226^\circ F.$), slightly soluble in water, freely in alcohol. *Para*.—Orange-colored needles or tables, melting at $146^\circ C.$ ($294.8^\circ F.$), nearly insoluble in water, easily soluble in alcohol.

Dinitranilines, $C_6H_3(NO_2)_2.NH_2$.—The unsymmetrical modification 1 : 2 : 4 (NH_2 in 1), is formed by heating the corresponding dinitro-, chloro-, bromo-, or iodo-benzene, or the methylic ether of (1 : 2 : 4) dinitrophenol with alcoholic ammonia, or dinitro-acetanilide with potash-lye. It crystallizes in light yellow prisms, melting at $182-183^\circ C.$ ($359.6-361.4^\circ F.$), does not combine with acids. By exchange of NH_2 for H it is converted into meta-dinitrobenzene.

Consecutive Dinitraniline (1 : 2 : 6), from the corresponding dinitro-iodobenzene or methyl-dinitrophenol, forms long, dark yellow needles, melting at $138^\circ C.$ ($280.2^\circ F.$), sparingly soluble even in hot alcohol.

Trinitraniline, $C_6H_2(NO_2)_3.NH_2$ (1 : 2 : 4 : 6) (*Picramide*), is formed by the action of alcoholic ammonia on trinitrochlorobenzene, $C_6Cl.NO_2.H.NO_2.H.NO_2$ (p. 831), or on the ethylic or methylic ether of picric acid. It crystallizes from alcohol in orange-red needles; from glacial acetic acid in large monoclinic tables; melts at $186^\circ C.$ ($366.8^\circ F.$). By heating with alkalis it is converted into a salt of picric acid :



Chloro- and Bromo-nitranilines, of which numerous modifications are known, are obtained by heating nitrodichloro- and nitrodibromobenzenes with alcoholic ammonia; by treating chlor- and brom-acetanilides with nitric acid, and decomposing the resulting nitro-compounds with alkalis; and by passing chlorine gas or bromine vapor into the solution of the three nitranilines in hydrochloric acid.

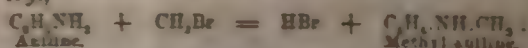
Diamidobenzenes, or Phenylenediamines, $C_6H_4(NH_2)_2$.—These bases are formed by reduction of the three dinitrobenzenes or the three nitranilines with tin and hydrochloric acid; also by dry distillation of the corresponding diamidobenzoic acids. They are bi-acid bases, forming well-defined crystalline salts; e. g., $C_6H_4(NH_2)_2.2HCl$.

Amidobenzene or **aniline**, $C_6H_5NH_2$, (1 : 2 : 4), melts at $105^\circ C.$ ($221.0^\circ F.$), boils at $184^\circ C.$ ($363.2^\circ F.$), dissolves in water, especially when hot. Its solution in hydrochloric acid is colored dark-red by ferric chloride or potassic iodide. *Meta*-amidobenzene melts, easily soluble in water, boils at $195^\circ C.$ ($393.0^\circ F.$), melts at $127^\circ C.$ ($260.6^\circ F.$). *Para*-amidobenzene is finely crystalline, easily soluble in water, melts at $147^\circ C.$ ($306.6^\circ F.$), boils at $267^\circ C.$ ($512.6^\circ F.$).

Triamidobenzene, $C_6H_3(NH_2)_3$, (1 : 2 : 4), is produced by dry distillation of triamidobenzene and mixed with powdered glass, and by reduction of (1 : 2 : 4) nitrobenzene with tin and hydrochloric acid. It forms a dark-red radi-crystalline mass, melting at $105^\circ C.$ ($217.4^\circ F.$), boiling at $238^\circ C.$ ($460.4^\circ F.$), easily soluble in water, alcohol and ether, separated from the aqueous solution by caustic soda. By ferric chloride and by strong sulphuric acid containing a little nitric acid, its solutions colored deep blue. It forms well-defined salts with acids.

ALCOHOLIC DERIVATIVES OF ANILINE.

The partial or total replacement of the hydrogen in the amidogen group of aniline by alcohol-radicles, gives rise to compounds analogous to the secondary and tertiary amines of the fatty group, and formed in the manner by heating aniline with the iodides and bromides of the alcohol-radicles, *e. g.*,



They may also be produced by heating aniline hydrochloride with alcohol in closed vessels, a chloride of the alcohol-radicle being first formed, which then acts as above on the aniline. The tertiary derivatives, such as diethylaniline, $C_6H_5N(C_2H_5)_2$, can also unite with alcoholic iodides, forming ammonium-compounds, like methyl-diethyl-phenylammonium, $(CH_3)(C_2H_5)_2(C_6H_5)N^+I^-$, which, when treated with moist silver oxide, yield the corresponding hydroxides, such as $(CH_3)(C_2H_5)_2(C_6H_5)N.OH$. These hydroxides are very soluble in water, strongly alkaline, and have a bitter taste.

The secondary and tertiary derivatives are liquid at ordinary temperatures, and exhibit the following physical properties:—

| | | Boiling Point. | Specific Gravity. |
|--------------------|-----------------------------|---|---|
| Methylaniline, | $C_6H_5NH(CH_3)$ | $190.0-191.0^\circ C.$
($374.37.0^\circ F.$) | 0.976 at $15^\circ C.$
($60.3^\circ F.$) |
| Dimethylaniline, | $C_6H_5N(CH_3)_2$ | $192.0^\circ C.$
($377.60^\circ F.$) | 0.9533 at $15^\circ C.$
($60.30^\circ F.$) |
| Ethylaniline, | $C_6H_5NH(C_2H_5)$ | $204.0^\circ C.$
($399.2^\circ F.$) | 0.954 at $15^\circ C.$
($60.40^\circ F.$) |
| Diethylaniline, | $C_6H_5N(C_2H_5)_2$ | $213.0^\circ C.$
($416.30^\circ F.$) | 0.938 at $15^\circ C.$
($60.4^\circ F.$) |
| Amylaniline, | $C_6H_5NH(C_4H_9)$ | $258.0^\circ C.$
($496.4^\circ F.$) | |
| Amyl-ethylaniline, | $(C_6H_5)N(C_4H_9)(C_2H_5)$ | $262.0^\circ C.$
($503.60^\circ F.$) | |

Dimethylaniline solidifies at $+0.5^{\circ}\text{C}$. (32.9°F). Amylethyl-aniline unites with methyl iodide, forming the iodide of methylethylamylphenylammonium, $(\text{C}_6\text{H}_5)_2\text{N}(\text{CH}_3)(\text{C}_5\text{H}_5)(\text{C}_6\text{H}_{11})$.

Many other alcoholic derivatives of aniline have been prepared and examined.

Diphenylamine, $\text{NH}(\text{C}_6\text{H}_5)_2$, is formed by heating aniline hydrochloride with aniline to 240°C . (464°F), and by the dry distillation of triphenyl-rosaniline (aniline blue). It is a crystalline body, having a pleasant odor, melting at 54°C . (129.2°F), and boiling at 310°C . (590°F), slightly soluble in water, easily in alcohol and ether; colored deep-blue by nitric acid. It is a weak base, its salts being decomposed by water.

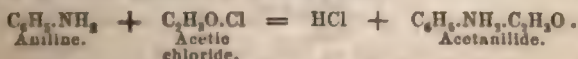
Triphenylamine, $\text{N}(\text{C}_6\text{H}_5)_3$, is produced, together with diphenylamine, by heating a solution of potassium in aniline with monobromobenzene.

Derivatives containing diatomic alcohol-radicles are formed by heating aniline with the iodides or bromides of methene and ethene. *Methene-diphenyldiamine*, $(\text{C}_6\text{H}_5.\text{NH})_2.\text{CH}_2$, is viscid and uncrystallizable. *Ethene-diphenyldiamine*, $(\text{C}_6\text{H}_5.\text{NH})_2.\text{C}_2\text{H}_4$, is crystalline, and melts at 57°C . (134.6°F). The isomeric *ethidine-diphenyldiamine*, $(\text{C}_6\text{H}_5.\text{NH})_2.\text{CH}=\text{CH}_2$, formed by the action of aldehyde on aniline, separates from alcoholic solution in yellowish nodules.

Derivatives containing tri-atomic alcohol-radicles are obtained by heating aniline with the chlorides of such radicles, or with substances capable of forming them. *Methenyl-diphenyldiamine*, $\begin{matrix} \text{C}_6\text{H}_5-\text{NH} \\ \text{C}_6\text{H}_5-\text{N} \end{matrix} \diagup \text{CH}$, produced by heating aniline with chloroform to $180^{\circ}\text{--}190^{\circ}\text{C}$. ($356\text{--}374^{\circ}\text{F}$) or by the action of phosphorus trichloride on a mixture of aniline and formanilide, crystallizes in long colorless needles, melting at $135^{\circ}\text{--}136^{\circ}\text{C}$. ($275^{\circ}\text{--}276.8^{\circ}\text{F}$), and boiling, with partial decomposition, above 250°C . (482°F). *Ethenyl-diphenyldiamine*, $\begin{matrix} \text{C}_6\text{H}_5-\text{NH} \\ \text{C}_6\text{H}_5-\text{N} \end{matrix} \diagup \text{C}=\text{CH}_2$, produced by the action of PCl_3 on a mixture of aniline and acetic acid, forms small colorless needles melting at $131^{\circ}\text{--}132^{\circ}\text{C}$. ($267.8^{\circ}\text{--}269.6^{\circ}\text{F}$).

DERIVATIVES CONTAINING ACID-RADICLES:—ANILIDES.

These compounds, which may be regarded as amides having their hydrogen more or less replaced by phenyl, are formed: 1. By the action of acid chlorides or chloranhydrides on aniline; thus:



2. By heating aniline salts with organic acids:



By heating with alkalis, or with hydrochloric acid, they are resolved into their components; e. g.,



Formanilide, $\text{C}_6\text{H}_5.\text{NH}.\text{CHO}$ —*Phenylformamide*.—Produced by

heating aniline with ethyl formate, or, together with other products, by quickly heating it with oxalic acid:



It forms prisms, melting at 49°C . (114.8°F .), easily soluble in water, alcohol, and ether. Strong soda-lye added to its aqueous solution throws down sodium formamide, $\text{C}_6\text{H}_5\text{NNA}=\text{CHO}$, when it is removed by water into formamide and sodium hydroxide. By distillation with strong ly. it is almost lost; it yields a small quantity of benzocitril $\text{C}_6\text{H}_5\text{NHCHO} = \text{C}_6\text{H}_5\text{CN} + \text{H}_2\text{O}$.

Acetanilide, $\text{C}_6\text{H}_5\text{NH.C}_2\text{H}_3\text{O}$, *Phenylacetamide*, produced by heating aniline and glacial acetic acid (1 mol. of each) for several hours, or by the action of acetyl chloride or acetic anhydride on aniline, forms colorless, shining laminar crystals, melting at 112°C — 113°C . (233.6° — 235.4°F .), solidifying without decomposition at 292°C . (558°F .), sparingly soluble in cold water, more easily in hot water and in alcohol. Treated with bromine, chlorine, or nitric acid, it yields mono- and di-substitution products, the substitution always taking place in the benzene ring, and those when heated with alkalis yield alcoholic anilines. *Monoacetylanilide*, $\text{C}_6\text{H}_4\text{Br}=\text{NH}(\text{C}_2\text{H}_3\text{O})$ (1:4), melts at 165°C . (329°F .); *diacetylanilide* at 149°C . (304.8°F .); *paraacetylanilide* melts at 207°C . (404.6°F .); *ortho-* at 78°C . (172.4°F .). *Triacetylanilide*, $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{NH}(\text{C}_2\text{H}_3\text{O})$, formed by dissolving acetanilide in a mixture of nitric and sulphuric acids, melts at 120°C . (248°F .).

Oxanilamide, $\begin{array}{c} \text{CO}-\text{NH}-\text{C}_6\text{H}_5 \\ | \\ \text{CO}-\text{NH}_2 \end{array}$, *Phenyloramide*, formed, together

with oxanilide, by evaporating cyananiline with hydrochloric acid, crystallizes in laminae, soluble in hot water, and subliming without decomposition.

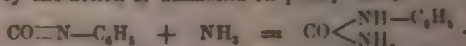
Oxanilide, $\begin{array}{c} \text{CO}-\text{NH}-\text{C}_6\text{H}_5 \\ | \\ \text{CO}-\text{NH}-\text{C}_6\text{H}_5 \end{array}$, *Diphenyloramide*, obtained by heating

aniline oxalate to 1600°C — 1800°C . (320° — 3560°F .), and together with oxanilamide, by evaporating a solution of cyananiline in hydrochloric acid, forms shining sublimable crystals, melting at 245°C . (473°F .).

Oxanillic Acid, $\begin{array}{c} \text{CO}-\text{NH}-\text{C}_6\text{H}_5 \\ | \\ \text{CO}-\text{OH} \end{array}$, produced by heating aniline

with excess of oxalic acid, forms crystalline scales slightly soluble in cold, easily in hot water, and having a strong acid reaction. It is monobasic.

Carbanilamide, $\text{CO} \begin{array}{c} \text{NH}-\text{C}_6\text{H}_5 \\ \text{NH}_2 \end{array}$, *Phenyl-carbamide*, *Phenyl-urea* is formed, like ethyl-carbamide (p. 791), by passing cyanic acid vapor into aniline, and by the action of ammonia on phenyl isocyanate (carbanil)



The easiest method of preparing it is to evaporate an aqueous solution of potassium cyanide and aniline sulphate. It forms colorless, needle-shaped crystals, melting at 144°C — 145°C . (291.2° — 293°F .), sparingly soluble in cold water, easily in hot water, and in alcohol and ether. Decomposed by heat into ammonia, cyanuric acid and carbanilide.

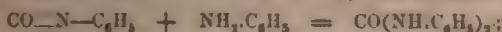
Alcoholic derivatives of phenylcarbamide, e. g., *ethyl-phenylcarbamide*,

$\text{CO} \begin{smallmatrix} \text{NH.C}_6\text{H}_5 \\ \text{NH.C}_6\text{H}_5 \end{smallmatrix}$, are formed by the action of aniline on isocyanic ethers (carbimides, p. 542).

Carbanilide, $\text{CO} \begin{smallmatrix} \text{NH.C}_6\text{H}_5 \\ \text{NH.C}_6\text{H}_5 \end{smallmatrix}$, *Diphenyl-carbanide*, *Diphenyl-urea* (symmetrical), is produced by the action of carbonyl chloride (phosgene) on aniline:



by combination of phenyl isocyanate (carbanil) with aniline:

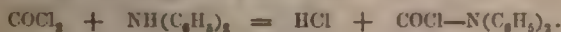


by heating 1 part of urea with 3 parts of aniline to $150^\circ\text{--}170^\circ\text{C}$. ($302^\circ\text{--}338^\circ\text{F}$.):



also by heating 1 mol. aniline with 1 mol. carbanilamide; and, together with formanilide, by the action of heat on oxanilamide. It forms silky needles, slightly soluble in water, moderately soluble in alcohol, melts at 235°C . (455°F .), and volatilizes without decomposition.

Chlorocarbanilide, $\text{COCl}-\text{N}(\text{C}_6\text{H}_5)_2$, is formed by passing phosgene gas into a solution of diphenylamine in chloroform:



It crystallizes in colorless laminae. With alcoholic ammonia it forms unsymmetrical diphenyl-carbamide:



which crystallizes in long needles, melting at 189°C . (372.2°F .). Heated with aniline, it yields triphenyl-carbamide, $\text{CO} \begin{smallmatrix} \text{NH.C}_6\text{H}_5 \\ \text{N}(\text{C}_6\text{H}_5)_2 \end{smallmatrix}$ (needles melting at 136°C . (276.8°F .)); and with diphenylamine at $200^\circ\text{--}220^\circ\text{C}$. ($392^\circ\text{--}428^\circ\text{F}$.) it forms tetraphenyl carbamide, $\text{CO}[\text{N}(\text{C}_6\text{H}_5)_2]_2$, light yellow crystals, melting at 183°C . (361.4°F .).

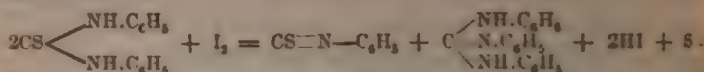
Carbanillo, or **Phenyl-carbamic Acid**, $\text{CO} \begin{smallmatrix} \text{NH.C}_6\text{H}_5 \\ \text{OH} \end{smallmatrix}$, is not known in the free state. Its ethers, the phenylurethanes, are formed by the action of alcohols on carbanil. The *ethylic ether*, $\text{CO} \begin{smallmatrix} \text{NH.C}_6\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$, produced also by the action of ethyl chlorocarbonate, $\text{COCl}.\text{OC}_2\text{H}_5$, on aniline, forms colorless needles melting at 52°C . (125.6°F .). It boils at $237^\circ\text{--}238^\circ\text{C}$. ($458.6^\circ\text{--}460.4^\circ\text{F}$.), with partial decomposition into alcohol and carbanil, and is converted, by heating with strong potash-lye, or with aniline, into diphenylcarbamide.

Carbanil, **Phenyl Isocyanate**, or **Phenyl carbimide**, $\text{CO}-\text{N}-\text{C}_6\text{H}_5$, formed by distilling oxanilide, or better, ethylic carbanilate, with phosphoric anhydride, is a mobile liquid, boiling at 163°C . (325.4°F .), and having a pungent, tear-exciting odor. Its reactions are exactly like those of the isocyanic ethers already described (p. 546). With water it forms carbanilide:



By ammonia it is converted into carbanilamide, and by amines into alcoholic derivatives of that compound. It unites with alcohols to form the carbanilic ethers.

Thiocarbanil, or **Phenyl-thiocarbimide**, $\text{CS}=\text{N}-\text{C}_6\text{H}_5$, also called *Phenyl Mustard-oil*, is formed from thiocarbamide by distillation with phosphoric anhydride, by prolonged boiling with hydrochloric acid, and, together with triphenylguanidine, by the action of iodine in alcoholic solution:



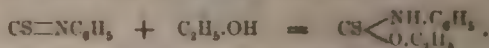
It is also produced by the action of phosgene on aniline. It is a colorless liquid, smelling like mustard-oil, boiling at 222°C . (431.6°F). By heating with reduced copper, it is converted into phenyl cyanide benzonitril:



Hydrogen sulphide passed into phenyl-thiocarbimide decomposes it, even at ordinary temperatures, into thiocarbamide and carbon bisulphide:



It unites with ammonia to form phenylthiocarbamide; with aniline, to form diphenylcarbamide; and with anhydrous alcohol at 120°C . (248°F), to form phenylic thiocarbamates or thiourethanes:



Normal Phenyl Thiocyanate, $\text{CN.S.C}_6\text{H}_5$, isomeric with thiocarbanil, is obtained by the action of cyanogen chloride on the lead-salt of phenyl-mercaptan:

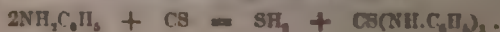


It is a colorless liquid which boils at 231°C . (447.8°F), and reacts like the normal thiocyanic ethers of the fatty series.

Thiocarbanilamide, or **Phenylthiocarbamide**, $\text{CS} \begin{cases} \text{NH.C}_6\text{H}_5 \\ \text{NH}_2 \end{cases}$,

formed by the combination of ammonia with thiocarbanil, crystallizes in needles, melting at 154°C . (309.2°F), slightly soluble in cold, more easily in boiling water and in alcohol. When boiled with silver nitrate it exchanges its sulphur for oxygen, and is converted into phenylcarbamide.

Thiocarbanilide, or **Diphenylthiocarbamide**, $\text{CS}(\text{NH.C}_6\text{H}_5)_2$, is formed by the action of carbon disulphide on aniline:

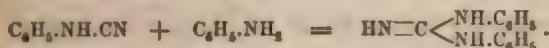


Aniline and potassium hydroxide, in equal numbers of molecules are heated for an hour in alcoholic solution with excess of carbon sulphide, the resulting liquid is poured into dilute hydrochloric acid, the alcohol evaporated, and the mass crystallized from alcohol.

Thiocarbanilide forms colorless laminae melting at 144°C . (291.2°F), insoluble in water, easily soluble in alcohol and ether. The mode of its conversion into phenylthiocarbimide and triphenyl-guanidine has been

already explained (p. 842). By treating it with alcoholic ammonia and lead oxide, the S is replaced by NH, and diphenyl-guanidine is produced.

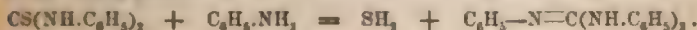
Diphenyl-guanidine, $\text{HN}=\text{C} \begin{smallmatrix} \text{NH.C}_6\text{H}_5 \\ \text{NH.C}_6\text{H}_5 \end{smallmatrix}$ (*Melaniline*), is also formed by the action of gaseous cyanogen chloride on dry aniline, and by boiling cyananilide with aniline hydrochloride:



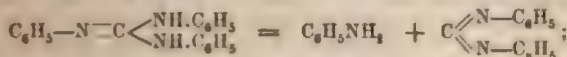
It forms long flattened needles, melting at 147°C . (296.6°F .), soluble in 10 parts of alcohol at ordinary temperatures, slightly soluble in water. It is a mono-acid base, and forms well-crystallized salts. When heated above its melting point, it is resolved into ammonia, aniline, and *tetra-phenyl-melamine*, $\text{C}_4\text{N}_4\text{H}_2(\text{C}_6\text{H}_5)_4$. By carbon disulphide it is converted into thiocarbamilide and thiocyanic acid:



Triphenyl-guanidine (α), $\text{C}_6\text{H}_5\text{—N}=\text{C} \begin{smallmatrix} \text{NH.C}_6\text{H}_5 \\ \text{NH.C}_6\text{H}_5 \end{smallmatrix}$, is formed by the action of heat on diphenyl-carbamide; by heating diphenyl-thiocarbamide either alone or with copper to $150\text{--}160^\circ \text{C}$. ($302\text{--}320^\circ \text{F}$.), or with aniline to the boiling point of the latter. It is most easily prepared by heating an alcoholic solution of diphenyl-thiocarbamide and aniline with lead oxide or mercuric oxide, or with an alcoholic solution of aniline to the boiling point:



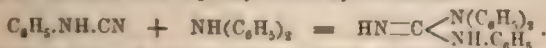
Triphenyl-guanidine crystallizes in shining rhombic prisms, melting at 143°C . (289.4°F .), nearly insoluble in water even at the boiling heat, easily soluble in hot alcohol. It is a mono-acid base, forming well-crystallized salts. By distillation it is resolved into aniline and diphenyl-cyanamide or carbodiphenylimide, which recombine in the receiver:



and by heating to $160\text{--}170^\circ \text{C}$. ($320\text{--}338^\circ \text{F}$.) with carbon disulphide, into phenyl-thiocarbamide and diphenyl-thiocarbamide:



An isomeric *triphenyl-guanidine* (β), $\text{HN}=\text{C} \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_5)_2 \\ \text{NH.C}_6\text{H}_5 \end{smallmatrix}$, is formed by heating cyananilide with diphenylamine hydrochloride:



It crystallizes in large tables melting at 131°C . (267.8°F .).

Tetraphenyl-guanidine, $\text{HN}=\text{C}[\text{N}(\text{C}_6\text{H}_5)]_2$.—The hydrochloride is formed by passing gaseous cyanogen chloride into fused diphenylamine heated to $160\text{--}170^\circ \text{C}$. ($320\text{--}338^\circ \text{F}$.). The free base separated therefrom by an alkali forms colorless rhombic prisms, melting at $130\text{--}131^\circ \text{C}$. ($266\text{--}267.8^\circ \text{F}$.).

Phenyl-cyanamide, or **Cyananilide**, $\text{CN.NH.C}_6\text{H}_5$, formed by passing gaseous cyanogen chloride into an ethereal solution of dry aniline, or by digesting an alcoholic solution of phenyl-thiocarbamide with lead

oxide, crystallizes in long needles, melting at 36° – 37° C. (96.8° – 98.6° F.), sparingly soluble in water, easily in alcohol and ether. It has no toxic properties, but unites with hydrogen sulphide to form phenylthiocarbamide, $\text{NH}_2\cdot\text{CS}\cdot\text{NH}(\text{C}_6\text{H}_5)$, and is converted spontaneously, even at ordinary temperatures, into the polymeric compound triphenylisocyanamine, $\text{C}_3\text{N}_6\text{H}_6(\text{C}_6\text{H}_5)_3$, which crystallizes in prisms melting at 162 – 163° C. (323.6 – 325.4° F.).

Diphenylcyanamide or Carbo-diphenylimide.

$\text{C}_{12}\text{H}_{10}\text{N}_2 = \text{C} \begin{smallmatrix} \text{N}-\text{C}_6\text{H}_5 \\ \text{N}-\text{C}_6\text{H}_5 \end{smallmatrix}$, is formed by adding mercuric oxide to a solution

of diphenylthiocarbamide in hot benzene, and, together with aniline is distilled off of α -triphenyl-guanidine. It is a syrupy liquid, boiling at 330 – 331° C. (626° – 627.8° F.), and changing, when kept in an exsiccator into a solid polymeric compound. Hydrochloric acid gas passed into a solution in hot benzene converts it into a crystalline hydrochloride, $\text{C}_{12}\text{H}_{10}\text{N}_2\cdot\text{HCl}$. By boiling with aqueous alcohol it is converted into diphenylcarbamide. It unites with SH_2 to form diphenylthiocarbamide, and with CS_2 at 140 – 150° C. (284° – 302° F.) to form phenylthiocarbimide, $\text{C}(\text{N}\cdot\text{C}_6\text{H}_5)_2 + \text{CS}_2 = 2(\text{CS}\cdot\text{N}-\text{C}_6\text{H}_5)$.

Cyananiline, $(\text{C}_6\text{H}_5\cdot\text{NH}_2)_2(\text{CN})_2 = \begin{smallmatrix} \text{C}(\text{NH})-\text{NH}\cdot\text{C}_6\text{H}_5 \\ | \\ \text{C}(\text{NH})-\text{NH}\cdot\text{C}_6\text{H}_5 \end{smallmatrix}$, separates on

passing cyanogen gas into an alcoholic solution of aniline, in shining laminae, melting at 210° C. (410° F.). It is a biacid base, and is resolved by boiling with acids into oxamide and oxanilide.

PHENYL PHOSPHORUS-COMPOUNDS.

Phosphenyl Chloride, $\text{C}_6\text{H}_5\cdot\text{PCl}_2$, formed by repeatedly passing a mixture of the vapors of benzene and phosphorus trichloride through a red-hot tube filled with fragments of pumice, and in small quantity by heating mercury-diphenyl with phosphorus trichloride, is a fuming, strongly refracting liquid, having a density of 1.319 at 25° C. (77° F.), and boiling at 222° C. (431.6° F.); decomposed by water into hydrochloric and phosphenylous acids. It unites with *chlorine* forming the tetrachloride, $\text{C}_6\text{H}_5\cdot\text{PCl}_4$, which melts at 73° C. (163.4° F.); with *bromine* to form $\text{C}_6\text{H}_5\cdot\text{PCl}_2\text{Br}_2$, melting at 208° C. (406.4° F.); with oxygen to form the oxychloride, $\text{C}_6\text{H}_5\cdot\text{PCl}_2\text{O}$, which is a liquid boiling, with partial decomposition, at 260° C. (500° F.); and with *acetic acid* to form $\text{C}_6\text{H}_5\cdot\text{PCl}_2\text{S}$, a liquid boiling, also with partial decomposition, at 276° C. (518° F.).

Phosphenylous Acid, $\text{C}_6\text{H}_5\cdot\text{PHO}\cdot\text{OH}$, formed, as above mentioned, by the action of water on the dichloride, crystallizes in colorless laminae, melting at 70° C. (158° F.), and acts as a powerful reducing agent. **Phosphophenyllic acid**, $\text{C}_6\text{H}_5\cdot\text{PO}(\text{OH})_2$, formed in like manner from the tetrachloride, crystallizes in laminae, melting at 158° C. (316.4° F.).

Phenyl-phosphine, $\text{C}_6\text{H}_5\cdot\text{PH}_2$.—Dry hydriodic acid gas passed into phosphenyl chloride unites with it, forming the compound $\text{C}_6\text{H}_5\cdot\text{PH}_2\cdot\text{HI}$, which is decomposed by alcohol, with formation of phenylphosphine. The latter is a liquid having a pungent and offensive odor, heavier than water,

boiling at 160°C . (320°F .). It oxidizes in the air, forming phosphenyl oxide, $\text{C}_6\text{H}_5\text{P}(\text{H})_2\text{O}$, a crystalline mass easily soluble in water. Phenylphosphine does not dissolve in aqueous acids, but unites with dry hydrogen iodide, forming phenylphosphonium iodide, $\text{C}_6\text{H}_5\text{P}(\text{H})_2\text{I}$, from which the phenylphosphine may be separated by water.

Diethyl-phenylphosphine, $\text{C}_6\text{H}_5\text{P}(\text{C}_2\text{H}_5)_2$, formed by the action of zinc-ethyl on phenylchloride, and treatment of the product with caustic soda, is a colorless strong-smelling liquid, having a specific gravity of 0.9571 at 13°C . (57.2°F .), boiling at 222°C . (431.6°F .), insoluble in water, soluble in acid, but not forming crystallizable salts. With ethyl iodide it forms the compound $\text{C}_6\text{H}_5\text{P}(\text{C}_2\text{H}_5)_2\text{I}$, which is crystalline, and easily soluble in water.

Arsenic Compounds.—*Arsenophenyl chloride*, $\text{C}_6\text{H}_5\text{AsCl}_2$, formed by the action of arsenious chloride on mercury-diphenyl, is a heavy colorless liquid, boiling at 252°C .– 255°C . (485.6° – 491°F .), not decomposed by water, soluble in alkalis. It unites with chlorine, forming a reddish-yellow liquid *tetrachloride*, $\text{C}_6\text{H}_5\text{AsCl}_4$, which is decomposed by water into hydrochloric and phenylarsinic acids, $\text{C}_6\text{H}_5\text{AsO}(\text{OH})_2$, crystallizing in long needles which melt at 168°C . (334.4°F .).

Arseno-diphenyl chloride, or *Phenylcacodyl chloride*, $(\text{C}_6\text{H}_5)_2\text{AsCl}$, formed in small quantity, together with the preceding compound, is a thick oil, boiling above 360°C . (690°F .), not decomposed by water. It unites with chlorine, forming the trichloride, $(\text{C}_6\text{H}_5)_2\text{AsCl}_3$, which melts at 174°C . (345.2°F .), and is decomposed by warm water into hydrochloric acid and phenylcacodylic acid, $(\text{C}_6\text{H}_5)_2\text{AsO.OH}$, which crystallizes in needles, slightly soluble in water, melting at 174°C . (345.2°F .).

Silico-phenyl Compounds.—The *chloride*, $\text{C}_6\text{H}_5\text{SiCl}_3$, obtained by heating mercury-diphenyl with silicic chloride, SiCl_4 , to 300°C . (572°F .), is a liquid which fumes in the air, and boils at 197°C . (386.6°F .). It is decomposed by water, with formation of silico-benzoic acid, $\text{C}_6\text{H}_5\text{SiO.OH}$, i. e., benzoic acid in which the C of the group COOH is replaced by Si. With alcohol, the triethylic ether, $\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$, is formed, as a liquid boiling at 237°C . (458.6°F .).

Mercury-diphenyl, $(\text{C}_6\text{H}_5)_2\text{Hg}$, is formed by heating a solution of bromobenzene in benzene for a considerable time with liquid sodium-amalgam, the reaction being facilitated by addition of a little acetic ether. It crystallizes in colorless rhombic prisms, melts at 120°C . (248°F .), and may be sublimed; turns yellow on exposure to the air; dissolves easily in benzene and carbon sulphide; less easily in ether and in alcohol; not at all in water. When distilled it is, for the most part, decomposed into diphenyl, benzene, and mercury. Acids decompose it, with formation of benzene and mercury salts. When treated with two molecules of chlorine, bromine, or iodine, it is decomposed into monochlorobenzene, etc., and a halogen-compound of mercury; e. g.:



With one molecule of the halogen element, haloïd-compounds are formed, like $\text{C}_6\text{H}_5\text{HgI}$, from which, by the action of moist silver oxide, the hydroxide, $\text{C}_6\text{H}_5\text{Hg.OH}$, is formed, a crystalline, strongly alkaline compound which expels ammonia from ammonium salts.

Amido-toluenes.

These, like other toluene derivatives, admit of metameric modifications, according as the NH_2 group is situated in the principal or the lateral chain (p. 813).

Toluidine, $\text{C}_7\text{H}_7\text{N} = \text{C}_6\text{H}_5(\text{NH}_2)\text{CH}_3$.—This base, homologous with aniline, exhibits the three modifications, ortho-, meta-, and para-, which are obtained by reduction of the three corresponding nitrotoluenes, $\text{C}_6\text{H}_4(\text{NO}_2)\text{CH}_3$.

Para-toluidine (ordinary toluidine), $\text{C}_6\text{H}_4\text{CH}_3\text{H.H.NH}_2\text{H}_2$, forms large colorless tabular crystals, heavier than water, very sparingly soluble in water, easily in alcohol and ether. It melts at 45°C . (113°F .), boils at 198°C . (388.4°F .); has an aromatic taste and odor, a very feeble alkaline reaction; does not give any colored reaction with chloride of lime. It forms crystalline salts, but is a weak base, incapable of neutralizing sulphuric acid. With acetyl chloride it forms acetoparatoluidine, $\text{C}_6\text{H}_4(\text{NH.C}_2\text{H}_5\text{O})\text{CH}_3$, a crystalline compound melting at 145°C . (293°F .).

Ortho-toluidine, also called *Pseudo-toluidine*, is a colorless, neutral liquid, becoming rose-colored on exposure to the air. It has a density of 1.00 at 16°C . (60.8°F .), boils at 199.5°C . (390.2°F .), and does not solidify at -20°C . (-4°F .). Its acetyl-derivative melts at 107°C . (224.6°F .).

Meta-toluidine, from metanitrotoluene, is a colorless liquid, of specific gravity 0.998 at 15°C . (59°F .), boiling at 197°C . (386.6°F .), not solidifying at -13°C . (8.6°F .). Its acetyl-derivative melts at 65.5°C . (149.9°F .).

Commercial toluidine, from aniline works, is a mixture of ortho- and para-toluidine, the latter of which partly crystallizes out on cooling to a low temperature. To separate the ortho-toluidine from the still dissolved para-modification, the liquid is heated with glacial acetic acid, whereby the two bases are converted into acetotoluides; these are dissolved in strong acetic acid, and the solution is diluted with 80 parts of water, whereby the acetoparatoluide is precipitated, while the acetorthotoluide remains in solution; or the mixture of the two bases is heated successively with oxalic acid and ether, whereby an oxalate of paratoluidine is first separated, the ortho-salt remaining dissolved.

Benzylamine, $\text{C}_6\text{H}_5\text{CH}_2(\text{NH}_2)$, or $\text{NH}_2(\text{C}_6\text{H}_5)$.—This compound, metameric with toluidine, is obtained, together with *dibenzylamine*, $\text{NH}(\text{C}_6\text{H}_5)_2$, and *tribenzylamine*, $\text{N}(\text{C}_6\text{H}_5)_3$, by the action of alcoholic ammonia on benzyl chloride, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (p. 826).

Benzylamine is a colorless liquid, boiling at 185°C . (365°F .). It mixes in all proportions with water, and is separated therefrom by potash. It is a much stronger base than toluidine; absorbs carbon dioxide rapidly, forming a crystalline carbonate; unites readily with acids, producing rise of temperature; and fumes with hydrochloric acid. The hydrochloride crystallizes in striated tables; the platinochloride, $2\text{NH}_2(\text{C}_6\text{H}_5)\text{Cl.PtCl}_4$, in orange-colored laminae.

Dibenzylamine, $(\text{C}_6\text{H}_5)_2\text{NH}$, is a colorless viscid liquid, insoluble in water, easily soluble in alcohol and ether; having a specific gravity of 1.033 at 14°C . (57.2°F .).

Tribenzylamine, $(C_6H_5)_3N$, forms colorless needles or laminæ, melting at $91^\circ C.$ ($195.8^\circ F.$), insoluble in water, slightly soluble in cold alcohol, easily in hot alcohol and in ether. Its hydrochloride, heated in a stream of dry hydrogen chloride, is resolved into benzyl chloride and the hydrochloride of dibenzylamine.

Diamidotoluenes or Tolylene-diamines, $C_6H_3(NH_2)_2$, CH_3 .—The modification 1 : 2 : 4 (CH_3 in 1), obtained by reduction of diminitrotoluene melting at $70.5^\circ C.$ ($158.9^\circ F.$), with tin and hydrochloric acid, crystallizes in long needles, melts at $99^\circ C.$ ($210.2^\circ F.$), and boils at $280^\circ C.$ ($536^\circ F.$). 1 : 3 : 4, obtained by reduction of metanito-paratoluidine, forms colorless scales, melting at $88.5^\circ C.$ ($191.3^\circ F.$), boiling at $265^\circ C.$ ($509^\circ F.$).

Metaxylylidine, $C_8H_{11}N = C_6H_3(NH_2).(CH_3)_2$, **Cumidine**, $C_9H_{13}N$, or probably $C_6H_4(NH_2).C_3H_7$, and **Cymidine**, $C_{10}H_{15}N$, or $C_{10}H_{13}(NH_2)$, homologous with toluidine, are obtained in like manner by reduction of the corresponding nitro-derivatives. Xylidine boils at 214° – $216^\circ C.$ (417.2° – $420.8^\circ F.$); cumidine at $225^\circ C.$ ($437^\circ F.$); cymidine at $250^\circ C.$ ($482^\circ F.$). Xylidine and cumidine form well-crystallized salts.

Mesidine or Amidomesitylene, $C_6H_2(CH_3)_3.NH_2$ (the three CH_3 -groups symmetrical, 1 : 3 : 5), is liquid. **Nitromesidine**, $C_6H_2(NO_2)(NH_2)$, melts at 100° ; **diamidomesitylene**, $C_6H_2(NH_2)_2$, at $90^\circ C.$ ($194^\circ F.$).

Xylylamine, $C_8H_{11}N = NH_2.C_6H_5 = C_6H_4(CH_3).CH_2NH_2$, homologous with benzylamine, is obtained, together with *di-xylylamine*, $NH(C_6H_5)_2$, and *tri-xylylamine*, $N(C_6H_5)_3$, by heating xylyl chloride, $C_6H_4(CH_3).CH_2Cl$, with alcoholic ammonia in sealed tubes. These three bases are oily liquids, smelling like herring-pickle, lighter than water, insoluble therein, easily soluble in alcohol and ether. Xylylamine boils at $196^\circ C.$ ($384.8^\circ F.$); di-xylylamine decomposes at $210^\circ C.$ ($410^\circ F.$).

Cumylamine, the 9-carbon base metameric with cumidine and homologous with benzylamine, has not been obtained.

Cymylamine, $C_{10}H_{15}N = NH_2(C_6H_{13}) = C_6H_4(CH_3).C_3H_6(NH_2)$, is obtained, together with *di-* and *tri-cymylamine*, by heating cymyl chloride with alcoholic ammonia in sealed tubes. Cymylamine and dicymylamine are oily liquids, boiling with decomposition, the former at $280^\circ C.$ ($536^\circ F.$), the latter above $300^\circ C.$ ($572^\circ F.$). *Tricymylamine* crystallizes in rhomboidal laminæ, melting at 81° – $82^\circ C.$ (177.8° – $179.6^\circ F.$).

ANILINE DYES.

Aniline has during the last few years found an extensive application in the arts, a long series of coloring matters unequalled in brilliancy and beauty having, by the action of different oxidizing agents, been produced from it. It was Mr. W. H. Perkin who first conceived the happy idea of applying practically the well-known property possessed by aniline, of forming violet and blue solutions when treated with a solution of chloride of lime or chromic acid. He succeeded in fixing these colors, and bringing them into a form adapted for the dyer.

Aniline-purple or Mauve, the first discovered of the aniline-dyes (1856), is prepared by mixing solutions of aniline sulphate and potassium bichromate in equivalent proportions, and allowing the mixture to stand for several hours. The black precipitate formed is filtered off and purified from admixed potassium sulphate by washing with water. It is then dried and freed from resinous matter by repeated digestion with castor naphtha, and finally dissolved in boiling alcohol. For its further purification, the alcoholic solution is evaporated to dryness, the substance is dissolved in a large quantity of boiling water, reprecipitated with caustic soda, washed with water, and dissolved in alcohol; and the filtered solution is evaporated to dryness. Mauve thus prepared forms a brittle substance, having a beautiful bronze colored surface: it is difficultly soluble in cold water, although it imparts a deep purple color to that liquid; it is more soluble in hot water, very soluble in alcohol, nearly insoluble in ether and hydrocarbons: it dissolves in concentrated acetic acid, from which it crystallizes. Mauve is the sulphate of a base called mauveine, having the composition $C_{20}H_{17}N_3$, and capable of forming crystalline salts with acids.

Aniline-red, Rosaniline, $C_{20}H_{19}N_3$ (or $C_{20}H_{17}N_3$).—Salts of this base occur more or less pure in commerce under the names *roseine*, *fuchsine*, *magenta*, *azaline*, etc. A red color had been observed at different times in experimenting with aniline, more especially when that substance was digested with Dutch liquid. The red coloring matter, though still impure, was first obtained in a separate state from the product formed by digesting aniline with carbon tetrachloride at $150^{\circ}C.$ ($302^{\circ}F.$), in which reaction it is formed, together with triphenylguanidine. Verguin (1858) first prepared it on a large scale by the action of stannic chloride upon aniline, and it has since been produced by the action of mercuric salts, arsenic acid, and many other oxidizing agents, upon aniline. The most advantageous mode of preparation is the following: A mixture of 12 parts of the dry arsenic acid which occurs in commerce, and 10 parts of aniline, is heated to 120° or $140^{\circ}C.$ (250° – $284^{\circ}F.$), with addition of water, for about six hours. The product, which is a hard mass having the lustre of bronze, is dissolved in hot water and precipitated by a slight excess of soda; the precipitate when washed with water, and dissolved in acetic acid, forms the roseine of commerce. In order to purify this still crude substance it is boiled with an excess of soda, to separate any aniline that it may contain; and the washed precipitate is dissolved in very dilute mineral acid, filtered from undissolved tarry matter, and reprecipitated with alkali. The compounds of rosaniline with one molecule of acid are beautifully crystallized substances, which in the dry state have a green color with golden lustre; with water they yield a very intensely colored red solution. The free base, first obtained by Nicholson, presents itself in colorless crystalline plates, insoluble in water, soluble in alcohol and ether, with a red color, which it also acquires on exposure to the air.

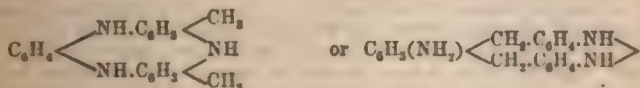
Rosaniline in the anhydrous state is represented by the formula, $C_{20}H_{19}N_3$, and in the hydrated state, such as it assumes when isolated from its compounds, by the formula $C_{20}H_{19}N_3 \cdot H_2O$. It is a triamine capable of forming monoacid, biacid, and triacid salts. The aniline-reds of commerce are monoacid salts of rosaniline, more or less pure. The acetate, which is chiefly found in commerce in England, has been prepared by Nicholson in splendid crystals of very considerable dimensions, having the composition $C_{20}H_{19}N_3 \cdot C_2H_3O_2$. In France the hydrochloride, $C_{20}H_{19}N_3 \cdot HCl$, is chiefly employed. The action of ammonium sulphide upon rosaniline gives rise to *leucaniline*, $C_{20}H_{21}N_3$, a base containing two additional atoms of hydrogen. This base is itself colorless, and forms colorless tri-

acid salts, such as $C_{20}H_{17}N_3 \cdot 3HCl$. Oxidizing agents reconvert it into rosaniline.

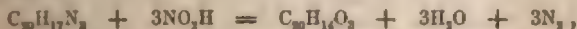
The molecular constitution of rosaniline has not been distinctly made out, and there is even some doubt (as above indicated) with respect to its empirical formula. Its mode of formation, also, is not thoroughly understood, but one very important fact has been brought to light by the researches of Hofmann, and confirmed by the experience of manufacturers—namely, that pure aniline, from whatever source it may be obtained, is incapable of furnishing aniline-red. Commercial aniline prepared from coal-tar always, in fact, contains toluidine as well as aniline; and Hofmann has shown that the presence of this base, together with aniline, is essential to the formation of the red dye. Toluidine by itself is just as incapable of yielding the red as pure aniline, but when a mixture of pure aniline and pure toluidine is treated with stannic or mercuric chloride, or with arsenic acid, the red coloring matter is immediately produced. If the formula $C_{20}H_{19}N_3$ be correct, the formation of rosaniline may perhaps be represented by the equation:



and its structure by the formula:



But rosaniline is converted by nitrous acid into aurin or rosolic acid, which, according to the recent experiments of Dale and Schorlemmer,* has the composition $C_{20}H_{14}O_3$, and is reconverted into rosaniline by heating with alcoholic ammonia. According to this, rosaniline should have the formula $C_{20}H_{17}N_3$, the two reactions just mentioned being represented by the equations:



and



Aniline Blue and Aniline Violet.—Girard and De Laire obtained aniline blue by digesting rosaniline with an excess of aniline at 150°C – 160°C . (302°F – 320°F). Together with aniline blue, which is the principal product of the reaction, several other coloring matters (violet and green), and indifferent substances, are formed, considerable quantities of ammonia being invariably evolved. The crude blue is purified by treating it successively with boiling water acidified with hydrochloric acid, and with pure water. The blue coloring matter is said to be obtained from its boiling alcoholic solution in brilliant needles. It consists of the hydrochloride of triphenyl-rosaniline, $C_{20}H_{16}(C_6H_5)_3$. By heating rosaniline with ethyl iodide, Hofmann has obtained an aniline violet, having the composition of hydriodide of triethyl-rosaniline, $C_{20}H_{16}(C_2H_5)_3N_3$. Another aniline violet is produced by heating rosaniline with a quantity of aniline less than sufficient to form aniline blue.

Other aniline violets are produced by the action of stannic chloride, mercuric chloride, or iodine chloride on methyl-aniline and dimethyl-aniline.

* Chem. Soc. Journal, 1877, vol. II. p. 121.

Aniline Greens—The most important of these colors are those known as "aldehyde green" and "iodine green." The former is produced by adding $1\frac{1}{2}$ parts aldehyde to a cold solution of magenta in a mixture of 3 parts strong sulphuric acid and 1 part water. The mixture is then heated in a water-bath till a drop of the product diffused in water produces a fine blue color, and then poured into a boiling solution of sodium thiosulphate. The liquid is then boiled for a short time and filtered. The filtrate contains the green, which may be precipitated by tannin or by sodium-acetate. Aldehyde green is principally used in silk-dyeing. It is a salt of an organic base which may be separated by means of soda or ammonia.

Iodine green is produced by heating the violets of triethyl- or trimethyl-rosaniline (Hofmann's violets) or the methyl-aniline violets, with iodide of methyl, ethyl, or amyl. The green thus obtained with methyl iodide has a very fine color, bluer than that of aldehyde green, and, like the latter, preserves its color by artificial light. It is much used for cotton and silk dyeing.

A third kind of aniline green, known commercially as "Perkin's green," resembles the iodine green, and is much used for calico-printing.

Chrysaniline, $C_{20}H_{17}N_3$ (or $C_{20}H_{15}N_3$?), is formed as a secondary product in the preparation of aniline red. It is a well-defined base, forming two series of salts, most of which are well crystallized. The two hydrochlorides of chrysaniline are $C_{20}H_{17}N_3.HCl$, and $C_{20}H_{15}N_3.2HCl$. The nitrate, $C_{20}H_{17}N_3.NO_3H$, is so little soluble in water that nitric acid may be precipitated even from a dilute solution of nitrates by means of the more soluble hydrochloride or acetate of chrysaniline.

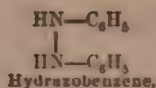
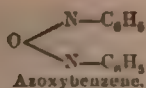
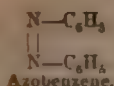
Aniline Brown is obtained by heating 4 parts of aniline hydrochloride to $240^\circ C.$ ($464^\circ F.$) with 1 part of aniline violet or aniline blue.

Aniline Black.—Blacks of great intensity are produced on calico by printing with a mixture of aniline, potassium chlorate, and a metallic compound—the one most generally used being cupric sulphide. The composition of aniline black is not known, neither is its mode of formation well understood; but it appears to depend upon oxidation of the aniline by the chlorate and the cupric sulphide, these compounds being thereby reduced, and afterwards reoxidized by the oxygen of the air, so that they act as carriers of oxygen. The finest black is obtained with vanadium salts, which easily undergo oxidation and reduction.

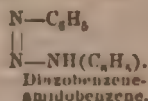
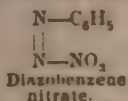
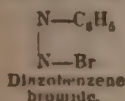
Aniline also forms coloring matters with xylidine. *Xylidine-rosaniline*, produced according to the equation $C_6H_7N + 2C_8H_{11}N = C_{22}H_{23}N_3 + 3H_2$, forms salts of a fine crimson color.

AZO- AND DIAZO-COMPOUNDS.

These compounds are derived from the aromatic hydrocarbons by substitution of 2 atoms of nitrogen for 2 atoms of hydrogen, the nitrogen apparently acting as a univalent radicle. In the azo-compounds the two nitrogen-atoms are united to one another by a part of their combining capacities, and each is directly combined with the carbon of a benzene-residue; thus:



In the diazo-compounds, only one of the nitrogen-atoms is directly linked to the carbon of a benzene-residue, while the free combining unit of the other is satisfied either by a halogen-element or by an acid residue, or generally in some way different from the first; thus:



The azo-compounds are formed: 1. By the action of certain reducing agents on the nitro-derivatives of the aromatic hydrocarbons; 2. By oxidation of aniline. They may, indeed, be regarded as stepping-stones from the nitro- to the amido-derivatives, as shown by the following formulæ:—

| | Equivalent formulæ. | | Molecular formulæ. |
|----------------------|-----------------------------------|-------|--|
| Nitrobenzene . . . | $\text{C}_6\text{H}_5\text{NO}_2$ | . . . | $\text{C}_6\text{H}_5\text{NO}_2$ |
| Azoxybenzene . . . | $\text{C}_6\text{H}_5\text{NO}_2$ | . . . | $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$ |
| Azobenzene . . . | $\text{C}_6\text{H}_5\text{N}$ | . . . | $\text{C}_{12}\text{H}_{10}\text{N}_2$ |
| Hydrazobenzene . . . | $\text{C}_6\text{H}_5\text{N}$ | . . . | $\text{C}_{12}\text{H}_{12}\text{N}_2$ |
| Amidobenzene . . . | $\text{C}_6\text{H}_7\text{N}$ | . . . | $\text{C}_8\text{H}_7\text{N}$ |

The hydrogen of the benzene-nucleus in these bodies may be partly replaced by the halogen-elements and the groups NO_2 , NH_2 , SO_3H , etc.

Azoxybenzene, $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$, or *Azoxybenzide*, is formed by the action of potash or soda, or of sodium-amalgam on nitrobenzene in alcoholic solution. Nitrobenzene (1 vol.) is dissolved in strong alcohol (8–10 vol.) and a quantity of dry potassium hydroxide, equal in weight to the nitrobenzene, is added; the liquid, which becomes heated spontaneously, is boiled for some time; the alcohol is then distilled off till the residual liquid separates into two layers; and the upper brown layer, which contains the azoxybenzene, is washed with water, whereupon it solidifies to a crystalline mass, which is recrystallized from alcohol.

Azoxybenzene forms long, yellow needles, insoluble in water, easily soluble in alcohol and ether. It melts at 36°C . (96.8°F .), and is decomposed by distillation into aniline and azobenzene. By reducing agents it is converted into azobenzene and hydrazobenzene. It yields two mononitro-derivatives, one melting at 143°C . (289.4°F .), the other at 49°C . (120.2°F .).

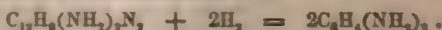
Azobenzene, $\text{C}_{12}\text{H}_{10}\text{N}_2$, *Azobenzide*, is formed by the action of iron and acetic acid, or better, of sodium-amalgam, on nitrobenzene. On heating the products, the azobenzene distils over as a yellow oil, which solidifies in the receiver, while azoxybenzene remains behind.

Azobenzene crystallizes in large yellowish-red laminæ, sparingly soluble in water, easily in alcohol and ether. It melts at 66.5°C . (151.7°F .) and distils at 293°C . (559.4°F .). By the action of ammonium sulphide and other reducing agents, it is converted into hydrazobenzene and the isomeric compound benzidine. With bromine it forms the compound $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{N}_2$, or $\text{C}_6\text{H}_5-\text{BrN}-\text{NBr}-\text{C}_6\text{H}_5$, and with nitric acid a mono- and a dinitro-derivative.

Amidazobenzene, or **Amidodiphenylimide**, $C_{12}H_9(NH_2)N_2 = C_6H_5-N=N-C_6H_4(NH_2)$.—This compound, which forms the chief constituent of commercial aniline yellow, is produced by the action of ammonium sulphide on nitro-azobenzene, and by a molecular transformation of the isomeric compound diazo-amidobenzene, $C_6H_5-N=N-NH(C_6H_5)$, which takes place when the latter is left in contact with alcohol and aniline hydrochloride; also by the action of sodium stannate and other oxidizing agents on aniline.

Amidazobenzene crystallizes from hot alcohol in yellow rhombic needles or prisms, sparingly soluble in hot water, melting at $127.4^\circ C.$ ($261.3^\circ F.$), and sublimable. It forms crystalline salts containing 1 equivalent of acid, yellow or violet in the solid state, decomposed by water. By distillation with sulphuric acid and manganese dioxide, it is oxidized to quinone, $C_6H_4O_2$. By the action of tin and hydrochloric acid, it is resolved into aniline and diamidobenzene.

Diamid-azobenzene, or **Diphenine**, $C_{12}H_9(NH_2)_2N_2$, formed by reduction of di-nitro-azobenzene with ammonium sulphide, is a yellow crystalline base, dissolving with red color in acids, resolved by reducing agents into two molecules of diamidobenzene:



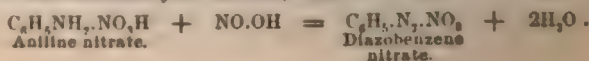
Hydrazobenzene, $C_{12}H_{11}N_2$, formed by the action of ammonium sulphide or sodium-amalgam on azobenzene or azoxybenzene, crystallizes in large plates, having a peculiar camphorous odor. It dissolves easily in alcohol and ether, but is insoluble in water; melts at $131^\circ C.$ ($267.8^\circ F.$). In contact with dilute mineral acids, it is easily converted into the isomeric compound, benzidine or diamidodiphenyl, $NH_2.C_6H_4-C_6H_4.NH_2$ (see DIPHENYL COMPOUNDS). By the action of oxidizing agents, or by contact of its alcoholic solution with the air, it is converted into azobenzene. By distillation it is resolved into aniline and azobenzene.

Diamidhydrazobenzene, $C_{12}H_{10}(NH_2)_2N_2$, produced by the action of sodium-amalgam on metanitr-aniline, forms yellow needles melting at $140^\circ C.$ ($284^\circ F.$).

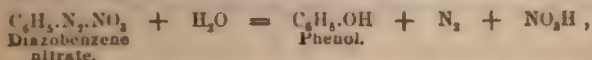
Azotoluene, $C_{14}H_{11}N_2$, formed by treating an alcoholic solution of nitrotoluene with sodium-amalgam, with occasional addition of acetic acid, crystallizes in orange-red shining needles, which melt at $137^\circ C.$ ($278.6^\circ F.$), and sublime without decomposition. It is insoluble in water, dilute acids and alkalis, but dissolves easily in alcohol and ether. Treated in alcoholic solution with sodium-amalgam or ammonium sulphide, it is converted into hydrazotoluene, $C_{14}H_{10}N_2$. With bromine it yields a crystalline addition-product, $C_{14}H_{11}BrN_2$.

Diazo Compounds.

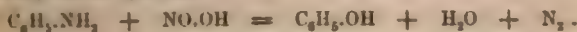
These compounds, the structure of which has been already explained, are formed by the action of nitrous acid on the salts of the amido-derivatives of the aromatic hydrocarbons; thus:



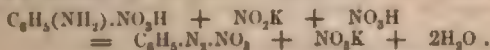
They are, however, somewhat unstable, and are apt to be decomposed by the water resulting from the reaction, especially if the liquid is hot, with evolution of nitrogen, and formation of hydroxyl-derivatives, *i. e.*, phenols:



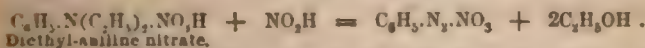
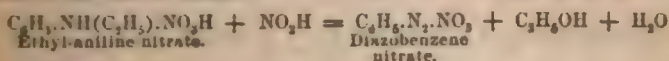
the final result being the same as if the nitrous acid acted on the aromatic amido-compound in the same way that it acts upon the amines and amides of the fatty series (p. 640):



A better mode of preparing the diazo-compound is to add solution of potassium nitrite to a solution of the amido-compound in nitric acid:

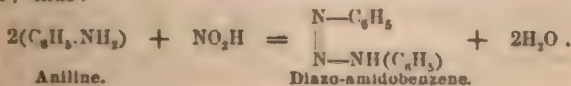


Amido-compounds in which the hydrogen of the NH_2 group is partly or wholly replaced by alcohol-radicles, generally yield the same diazo-compounds as the original amido-derivatives, the alcohol-radicles being separated in the form of alcohols:

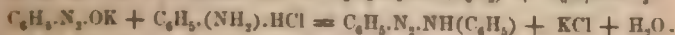
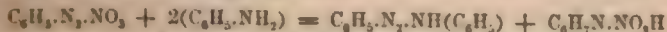


Those, on the contrary, in which the hydrogen of the benzene-nucleus is partly replaced by Cl, Br, NO_2 , etc., yield substituted diazo-compounds, such as $\text{C}_6\text{H}_4\text{ClN}_2\text{NO}_3$, $\text{C}_6\text{H}_4(\text{NO}_2)\text{N}_2\text{NO}_3$, etc.

When nitrous acid acts upon an amido-compound in the free state in alcoholic or ethereal solution, the product is a diazo-amido-compound; thus:

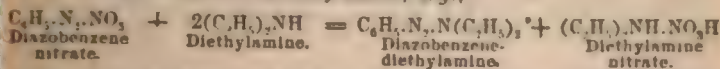


These compounds are also formed by the action of amines or their salts on the salts of diazo-compounds:



By this reaction, also, mixed diazo-amido-compounds may be obtained; for example, diazotoluene-amidobenzene, $\text{C}_7\text{H}_7\text{N}_2\text{NH}\cdot\text{C}_6\text{H}_5$, from toluidine and a salt of diazobenzene.

In like manner, diazo-amido-compounds may be formed with the primary and secondary amines of the fatty series; *e. g.*,



The diazo-compounds are mostly colorless crystalline bodies, which quickly turn brown on exposure to the air. They dissolve easily in water, sparingly in alcohol, and are precipitated from the alcoholic solutions by ether. Most of them are very unstable, and decompose with explosion

when heated or struck. They suffer decomposition also under the influence of the most various reagents, generally in such a manner that both the nitrogen-atoms are eliminated in the gaseous form, and the diazo-group is replaced by halogen elements, hydrogen, hydroxyl, etc.

1. When boiled with water, they yield phenols:



With *hydrogen sulphide* in like manner they yield mercaptans.

2. On boiling them with strong *alcohol*, the N_2 -group is replaced by hydrogen, producing benzene or a homologous hydrocarbon, while the alcohol is oxidized to aldehyde:



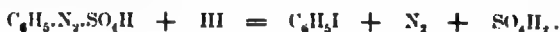
3. The *platinoclides*, formed by combination of the diazo chlorides with PtCl_4 , are decomposed when heated alone, or better with dry sodium carbonate and common salt, producing chlorinated hydrocarbons, which distil over:



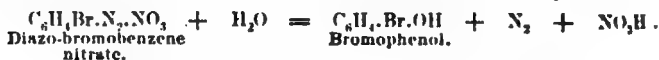
4. The *diazobromides* take up two atoms of bromine, forming perbromides, such as $\text{C}_6\text{H}_5\text{N}_2\text{Br}_2$ or $\begin{array}{c} \text{BrN—C}_6\text{H}_5 \\ | \\ \text{BrN—Br} \end{array}$, which are likewise decomposed by dry distillation, or more readily by boiling with strong alcohol, yielding monobromo-derivatives of the hydrocarbons:



5. The sulphates and other oxy-salts of the diazo-compounds, boiled with *hydriodic acid*, yield iodine-derivatives:



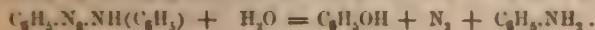
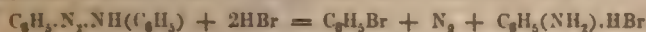
Diazo-compounds containing chlorous radicals (Cl , Br , NO_2 , etc.) in the benzene-nucleus undergo exactly similar decomposition; *v. g.*,



The reactions 1, 3, 4, and 5 afford the means of converting an aromatic amido-derivative (and therefore also a nitro-derivative), through the medium of the diazo-compound, into the corresponding halogen- and hydroxyl-derivatives; and this mode of transformation, known as the "diazo-reaction" serves, as already shown in several instances, to determine the relative positions of the substituted radicals in these derivatives (p. 823).

The diazo-amido-compounds, which may be regarded as formed by the union of diazo- and amido-derivatives, undergo similar transformations. They are first resolved, under the influence of hydrobromic or hydrochloric acid, etc., into their components, a diazo- and an amido-derivative; the

later than separates out either in the free state, or as a salt, and the diazo-compound is transformed in the manner above described; thus:



Diazobenzene-compounds.—The *nitrate*, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{NO}_3$, is prepared by passing nitrous acid vapor into a flask containing aniline nitrate moistened with a small quantity of water and cooled with ice, till the whole is dissolved, and the solution no longer yields aniline when mixed with potash. On filtering the liquid, and adding alcohol and ether, the diazobenzene nitrate separates as a crystalline mass, which may be purified by redissolution in a small quantity of cold water, and precipitation by alcohol and ether.

Diazobenzene nitrate forms long colorless needles, extremely soluble in water, slightly soluble in alcohol, insoluble in ether and in benzene. It is tolerably permanent when dry, but gradually turns brown on exposure to moist air. It explodes violently when heated.

The *sulphate*, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{SO}_4\text{H}$, is prepared by passing nitrous acid into aniline sulphate dissolved in water containing sulphuric acid, or better, by decomposing the nitrate with sulphuric acid. It forms colorless needles or prisms easily soluble in water, exploding at 100° .

The *bromide*, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{Br}$, separates in white laminae on gradually adding bromine dissolved in ether to an ethereal solution of diazo-amidobenzene while tribromaniline, which is formed at the same time, remains in solution.

The *perbromide*, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{Br}_3$, is formed by mixing an aqueous solution of the nitrate with a solution of bromine in hydrobromic acid or sodium bromide, and separates as a dark-brown oil, which soon solidifies to a crystalline mass. When recrystallized by solution in cold alcohol, and rapid evaporation in a vacuum, it may be obtained in large yellow laminae, insoluble in water and ether, moderately soluble in cold alcohol. By prolonged washing with ether, it is converted into the monobromide.

The *chloride*, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{Cl}$, is obtained in solution by agitating a solution of the bromide with moist silver chloride.

The *platinochloride*, $(\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{Cl})_2\cdot\text{PtCl}_4$, is precipitated in yellow prisms on adding a solution of platonic chloride to a solution of the nitrate or sulphate.

Diazobenzene-potassium, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{OK}$, separates on adding caustic potash to a solution of the nitrate, as a yellow liquid, which, when evaporated over the water-bath, crystallizes in white nacreous laminae, easily soluble in water and in alcohol. The aqueous solution quickly decomposes, and, when mixed with silver nitrate, yields a gray precipitate of $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{OAg}$, and similar precipitates with mercury, lead, zinc, and other metals. On adding acetic acid to a solution of the potassium-compound, a heavy oil is precipitated, probably consisting of diazobenzene hydroxide, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{OH}$.

Diazo-amidobenzene, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, is formed by the action of nitrous acid on aniline dissolved in alcohol; also by mixing a solution of diazobenzene nitrate with aniline; and by gradually pouring a cooled, slightly alkaline solution of sodium nitrite on aniline hydrochloride. It crystallizes in golden-yellow shining laminae, melts at 91°C . (195.8°F .), and detonates at a higher temperature. It is insoluble in water, easily soluble in ether, benzene, and hot alcohol. By nitric acid containing nitrous acid, it is converted into diazobenzene nitrate; by strong hydrochloric acid, into aniline hydrochloride, phenol, and nitrogen.—The alco-

holic solution mixed with silver nitrate deposits the compound $C_6H_5N_3$, $NAg.C_6H_5$, in reddish needles.

Diazo-amidobenzene does not unite with acids, but its alcoholic solution mixed with a solution of platinum chloride in hydrochloric acid, yields the platinumchloride, $(C_6H_5N_3.HCl)_2.PtCl_6$, in reddish needles.

Diazo-amidobenzene in alcoholic solution, especially if in contact with a small quantity of aniline hydrochloride, gradually changes into the isomeric compound, amidazobenzene, $C_6H_5.N=N.C_6H_5.NH_2$ (p. 862).

Diazobenzene-dimethylamide, $C_6H_5.N_2.N(CH_3)_2$, formed by mixing the aqueous solutions of diazobenzene nitrate and dimethylamine, is a yellow, oily liquid, having weak basic properties, and forming unstable salts, which in aqueous solution are easily resolved into phenol, nitrogen, and salts of dimethylamine.

Diazobenzene-ethylamide, $C_6H_5.N_2.NH(C_2H_5)$, resembles the dimethyl compound, and is formed in a similar manner.

Diazobenzeneimide, $C_6H_5.N_2$, probably $C_6H_5-N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} N$ is formed by

the action of aqueous ammonia on diazobenzene perbromide:



It is a yellow oil, insoluble in water, distilling without decomposition in rarefied air and in vapor of water, dissolving without alteration in nitric and sulphuric acid. Treated in alcoholic solution with zinc and hydrochloric acid, it is resolved into ammonia and aniline:



The diazo-compounds of higher orders, e. g., diazotoluene nitrate, $C_7H_7.N_2.NO_2$, diazo-amidotoluene, $C_7H_7.N_2.NH.C_7H_7$, etc., are analogous to the diazo-benzene compounds; but they have not been much examined.

HYDRAZINE-COMPOUNDS.

Phenyl-hydrazin, $C_6H_5N_2 = C_6H_5-NH-NH_2$.—When diazobenzene nitrate is added to a cold solution of acid potassium sulphite, the liquid solidifies to yellow crystals of potassium diazobenzene sulphonate, $C_6H_5N_2SO_3K$, or $C_6H_5-N=N-SO_3K$; this salt, heated on the water-bath with excess of acid potassium sulphite, is converted into colorless phenyl hydrazinsulphonate, $C_6H_5-NH-NH-SO_3K$, which is also formed by heating the former salt with zinc-dust and hydrochloric acid; and this colorless salt heated with hydrochloric acid yields the hydrochloride of phenyl-hydrazin, according to the equation:



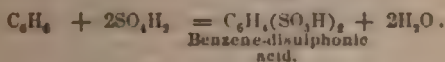
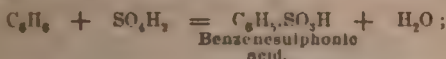
It is more easily obtained (together with aniline or diethylamine), by treating an alcoholic solution of diazo-amidobenzene or diazobenzene-diethylamine with zinc-dust and acetic acid.

Phenyl-hydrazin is a yellow oil, which solidifies at low temperatures to a crystalline mass, melting at $23^\circ C.$ ($73.4^\circ F.$), and boiling at $233^\circ-234^\circ C.$ ($451.4^\circ-453.2^\circ F.$). It dissolves sparingly in cold water, more readily in hot water, very easily in alcohol and ether. It possesses strong reducing properties, and is a mono-acid base, forming well-crystallized salts. Its hydrochloride, treated with potassium nitrite, yields the nitroso-

compound, $C_6H_5.N(NO).NH_2$, which, when heated with water, is converted into diazobenzonimide, $C_6H_5.N_2$. The nitroso-compound, treated with phenol and strong sulphuric acid, yields a brown solution changing to green and blue (Liebermann's reaction, p. 863).

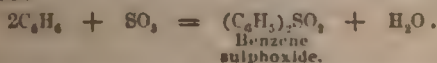
SULPHO-DERIVATIVES.

The sulpho-acids of the aromatic hydrocarbons are easily formed by the direct action of sulphuric acid, concentrated or fuming, on these hydrocarbons; thus:

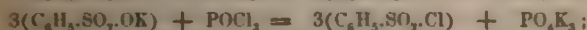
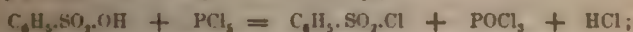


In this respect they differ from the sulpho-acids of the fatty group, which can be formed only from sulphites or from thio-alcohols (p. 554).

The aromatic hydrocarbons treated with sulphuric anhydride yield sulphoxides:



The sulpho-acids treated with phosphorus pentachloride, or their salts treated with the oxychloride, yield the sulphochlorides or chloro-anhydrides of the sulphonic acids; *e. g.*,



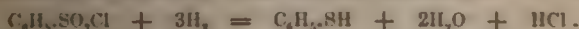
and the sulphochlorides treated with sodium-amalgam in ethereal solution, are converted into sulphinic acids (p. 555):



The sulphinic acids, or rather their zinc-salts, are also formed by the action of the zinc-compounds of the alcohol-radicles on the sulpho-chlorides, *e. g.*,



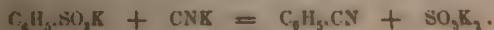
By zinc and hydrochloric acid, on the other hand, the sulpho-chlorides are reduced to hydrosulphides or thiophenols:



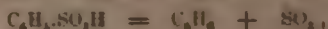
The aromatic sulpho-acids, like those of the fatty group, are very stable compounds, not decomposed by boiling with alkalis. By fusion with caustic alkalis they yield phenols:



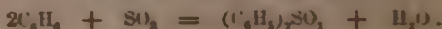
By distillation with potassium cyanide (or the dry ferrocyanide), they yield nitrile:



The free acids subjected to dry distillation yield hydrocarbon benzene-sulphoxide, or its homologues, being formed at the same time



and



The sulphonic acids of the substituted hydrocarbons are obtained by the action of sulphuric acid on these bodies, or by the action of halo-nitric acid, on the sulpho-acids of the primary hydrocarbons; in the latter case the sulpho-group is also frequently replaced. The sulpho-acid may also be replaced by chlorine, by heating a sulpho-acid or sulphide with phosphorus pentachloride:



Benzenesulphonic Acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, is produced by the action of sulphuric acid on benzene, or by the action of nitric acid on benzene, and then shaking it up with water, as a colorless oil; its specific gravity is 1.378 at 23°C . (73.4°F .), boiling with partial decomposition at $246^\circ\text{--}247^\circ\text{C}$. ($474.8^\circ\text{--}476.6^\circ\text{F}$.), and solidifying into large rhombic crystals. Boiling water slowly decomposes it into benzenesulphonic and hydrochloric acids.

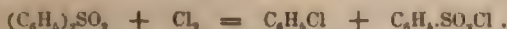
Benzenesulphochloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, separates, on gently shaking, as an intimate mixture of sodium benzenesulphonate and phosphorus pentachloride, and then shaking it up with water, as a colorless oil; its specific gravity is 1.378 at 23°C . (73.4°F .), boiling with partial decomposition at $246^\circ\text{--}247^\circ\text{C}$. ($474.8^\circ\text{--}476.6^\circ\text{F}$.), and solidifying into large rhombic crystals. Boiling water slowly decomposes it into benzenesulphonic and hydrochloric acids.

Benzenesulphamide, $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$, formed by treating the chloride with ammonia or ammonium carbonate, crystallizes from benzene in nacreous laminae melting at 148°C . (300.2°F .). Silver nitrate added to its alcoholic solution throws down the compound $\text{C}_6\text{H}_5\text{SO}_2\text{NHSg}$.

Benzenesulphinic, or Benzenesulphurous Acid, $\text{C}_6\text{H}_5\text{SO}_2\text{H}$, formed by the action of sodium-amalgam on the ethereal solution of benzenesulphonic acid, crystallizes from hot water in large shining plates, easily soluble in alcohol and ether, melting at 69°C . (156.2°F .), decomposing at 100° . With chlorine or bromine it forms benzene-sulphonic chloride or bromide, and is converted slowly by exposure to air, or quickly by oxidizing agents, into benzenesulphonic acid. This acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, is slightly soluble in water.

Phenyl Sulphoxide, or Sulphobenzide, $(\text{C}_6\text{H}_5)_2\text{SO}$, is formed by dry distillation of benzenesulphonic acid, by oxidation of phenyl sulphide, $(\text{C}_6\text{H}_5)_2\text{S}$, and by the action of fuming sulphuric acid or sulphuric anhydride on benzene. It is very slightly soluble in water, crystallizes in alcohol in plates, melts at $128^\circ\text{--}129^\circ\text{C}$. ($262.4^\circ\text{--}264.2^\circ\text{F}$.), and without decomposition. By heating with strong sulphuric acid, it

verted into benzenesulphonic acid, $(C_6H_5)_2SO_2 + SO_2H_2 = 2(C_6H_5.SO_2H)$; and when heated with phosphorus pentachloride or in a stream of chlorine, it is decomposed, with formation of chlorobenzene and benzenesulphochloride:—

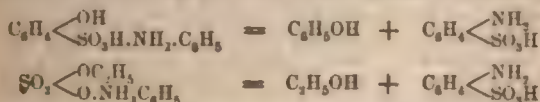


The action of chlorine in sunshine also converts it into chlorobenzene and its products of addition.

Phenyldisulphoxide, $(C_6H_5)_2S_2O_2$, produced, together with benzenesulphonic acid, by heating benzenesulphonic acid with water to $130^\circ C.$ ($266^\circ F.$), crystallizes in long shining needles, melting at 100° , insoluble in water, easily soluble in alcohol and ether.

Chloro-, Bromo-, Iodo-, Nitro-, and Amido-benzenesulphonic Acids, $C_6H_4Cl.SO_2H$, etc.—The sulpho-acids formed by dissolving C_6H_5Cl , C_6H_5Br , C_6H_5I , and $C_6H_5NH_2$, in slightly fuming sulphuric acid, belong chiefly to the para-series (1 : 4), e. g., $C_6H_4Cl.SO_2H.H.H.Br.H_2$; nitrobenzene, on the other hand, yields by similar treatment a product consisting also wholly of *meta*-nitrobenzenesulphonic acid, $C_6H_3(NO_2).SO_2H.H_2$. The action of bromine or nitric acid on benzenesulphonic acid yields likewise a product consisting chiefly of the meta-acid. All these bodies are strong monobasic acids, which mostly crystallize well, dissolve easily in water, and yield well-crystallized salts, chlorides, and amides.

Para-amidobenzenesulphonic acid, long known by the name of sulphamitic acid, is produced by the action of sulphuric acid on aniline, also by distillation of phenolsulphate or of ethylsulphate of aniline:



It crystallizes from water in rhombic tables containing one mol. H_2O ; yields, by oxidation with chromic acid or with manganese dioxide and sulphuric acid, a large quantity of quinone, $C_6H_4O_2$; and is converted by nitrous acid into diazobenzene-sulphonic acid, $C_6H_4 \begin{array}{c} SO_2 \\ \diagup \quad \diagdown \\ N-N \end{array}$, which crystallizes from hot water in colorless needles; detonates with great violence, and is converted into benzenesulphonic acid by heating with absolute alcohol, and into sulphamic acid by the action of hydrogen sulphide.

Benzenedisulphonic Acids, $C_6H_4 \begin{array}{c} SO_3H \\ \diagup \quad \diagdown \\ SO_3H \end{array}$.—The *meta*- and *para*-modifications of this acid are obtained by heating benzenesulphonic acid with fuming sulphuric acid, or more readily by passing benzene vapor into ordinary sulphuric acid heated to $240^\circ C.$ ($464^\circ F.$). They are both very soluble in water, but may be separated by fractional crystallization of their potassium salts. The *meta*-acid, which is the principal product, yields a chloride, $C_6H_4(SO_2Cl)_2$, melting at $63^\circ C.$ ($145.4^\circ F.$), and an amide, $C_6H_4(SO_2NH_2)_2$, melting at $229^\circ C.$ ($444.2^\circ F.$). By distillation with potassium cyanide, it yields a dicyanide, $C_6H_4(CN)_2$, melting at $156^\circ C.$ ($312.8^\circ F.$), and convertible by the action of alkalis into metaphthalic or isophthalic acid, $C_6H_4(COOH)_2$.

Para-benzenedisulphonic acid forms a chloride melting at $131^\circ C.$ ($267.8^\circ F.$), and an amide melting at $288^\circ C.$ ($550.4^\circ F.$). By distillation with

potassium cyanide it yields a dicyanide, melting at 222°C . (431.6°F .), and convertible into terephthalic acid, $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ (1 : 4).

Benzenetrisulphonic Acid, $\text{C}_6\text{H}_3(\text{SO}_3\text{H})_3$.—The only known modification of this acid is obtained by heating a mixture of 10 parts benzene, 70 fuming sulphuric acid, and 40 phosphoric anhydride in sealed tubes to 280° – 290°C . (536° – 554°F .). Separated from its lead salt by hydrogen sulphide, it crystallizes in long flat needles containing 3 mol. H_2O .^{*}

Toluenesulphonic Acids, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$.—The *para*- and *ortho*-modifications are produced simultaneously by dissolving toluene in slightly fuming sulphuric acid, and may be approximately separated by fractional crystallization of their potassium salts, the *para*-salt separating out first, and crystallizing easily in large transparent six-sided tables or prisms containing 1 mol. H_2O . The *ortho*-salt separates from the mother-liquor mixed with *para*-salt, from which it is not easily purified. The *para*-acid crystallizes in deliquescent scales containing 1 mol. H_2O . Its *chloride*, $\text{C}_6\text{H}_5(\text{SO}_2\text{Cl})_2$, melts at 69°C . (156.2°F .). The *amide*, $\text{C}_6\text{H}_5(\text{SO}_2\text{NH}_2)_2$, at 137°C . (278.6°F .). Fused with potash it yields *para*-cresol, $\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$, and a small quantity of *para*-oxybenzoic acid.—The *ortho*-acid, which may be obtained pure by decomposing its *amide* with nitrous acid, is liquid. Its *amide* crystallizes from hot alcohol in shining octohedrons, melting at 153° – 154°C . (307.4° – 309.2°F .). The acid fused with potash yields *ortho*-cresol and *ortho*-oxybenzoic (*salicylic*) acid.

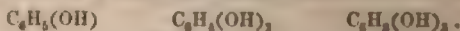
Metatoluenesulphonic acid, $\text{C}_6\text{H}_4\text{CH}_3\text{H}\text{SO}_3\text{H}\text{H}_2$, is obtained by the action of sodium-amalgam on the *ortho*-chloro- (or bromo-) toluene-sulphonic acid, $\text{C}_6\text{H}_4\text{CH}_3\text{Br}\text{SO}_3\text{H}\text{H}_2$, which is formed by dissolving *ortho*-chloro- (or bromo-) toluene in sulphuric acid. It is crystalline. Its *chloride* is a liquid not solidifying at -10°C . (14°F .); the *amide* is crystalline, and melts at 91° – 92°C . (195.8° – 197.6°F .).

A large number of substituted toluenesulphonic acids have been obtained by dissolving chlorotoluene, bromotoluene, etc., in sulphuric acid. *Para*- and *ortho*-toluenesulphonic acid heated with fuming sulphuric acid yield two modifications of toluenedisulphonic acid, $\text{C}_6\text{H}_3(\text{SO}_3\text{H})_2\text{CH}_3$.

Benzylsulphonic Acid, $\text{C}_6\text{H}_5\text{CH}_2(\text{SO}_3\text{H})$.—The potassium-salt of this acid is formed by heating benzyl chloride with a strong solution of potassium sulphite.

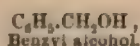
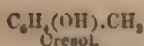
AROMATIC ALCOHOLS.

The substitution of OH for H in benzene gives rise to mono-, di-, and tri-atomic derivatives of alcoholic character, viz. :

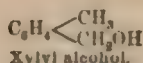
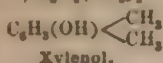


In toluene and the higher homologues of benzene the substitution may take place either in the principal or in the lateral chains, giving rise to metameric compounds: thus from toluene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$, are derived

^{*} Koerner e Monsellie, *Gazetta chimica Italiana*, 1876, p. 183.



and from xylene, $\text{C}_6\text{H}_4(\text{CH}_3)_2$:

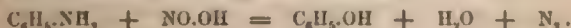


Those compounds in which the substitution takes place in the lateral chains, are primary alcohols, containing the group CH_2OH , and, like the corresponding alcohols of the fatty series, are convertible by oxidation into aldehydes and acids containing the same number of carbon-atoms, and readily exchange their OH group for Cl, Br, NH_2 , etc., giving rise to haloïd derivatives and amines. Those, on the other hand, in which the OH is situated in the principal chain, are not convertible by oxidation into aldehydes, ketones, or acids, in which respect they are analogous to the tertiary alcohols.

These latter compounds, including the hydroxyl-derivatives of benzene, are called Phenols. They are susceptible of isomeric modifications, according to the orientation of the substituted radicles in the benzene-nucleus.

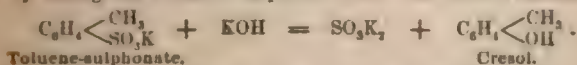
Monatomic Phenols.

These compounds are produced: 1. By the action of nitrous acid on aniline and its homologues in aqueous solution:



2. By decomposing the diazo-compounds with water, the sulphates being the best adapted for the purpose (p. 854).

3. By fusing the aromatic sulphonic acids with caustic alkalis:



4. By distilling the salts of aromatic oxy-acids with lime.



5. By the dry distillation of complex organic substances, such as wood and coal.

The phenols exhibit acid as well as alcoholic characters. When treated with metallic oxides, especially those of the alkali-metals, they readily exchange their hydroxylic hydrogen for metals, forming metallic salts, and these, when acted upon by alcoholic iodides are converted into phenolic ethers; e. g.,



Phenolic ethers containing acid-radicles, such as $\text{C}_6\text{H}_5.\text{O}.\text{OC}_2\text{H}_5$, are formed by the action of the chlorides of such radicles on the phenols and their metallic derivatives.

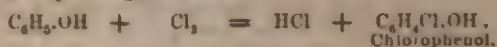
By the action of the halogen-compounds of phosphorus, the phenols are converted, by exchange of their OH-group for Cl, Br, etc., into halogen-

derivatives of hydrocarbons, such as C_6H_5Cl . By phosphorus pentasulphide, they are converted into thiophenols:

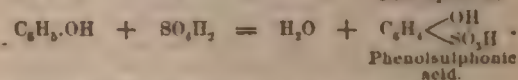


By heating with zinc-dust they are reduced to hydrocarbons.

By treatment with chlorine, bromine, iodine, nitric acid, and sulphuric acid, the phenols are converted into halogen-, nitro-, and sulpho-derivatives, by exchange of one or more atoms of hydrogen in the benzene-nucleus for Cl, Br, I, NO_2 , or SO_3H ; thus:



Chlorophenol.



Phenolsulphonic acid.

Phenols treated with metallic sodium and carbon dioxide are converted into salts of aromatic oxy-acids:



Phenol.

Oxybenzoic acid.

The monatomic phenols at present known contain 6, 7, 8, and 10 atoms of carbon.

Six-carbon Phenol, or simply Phenol, $C_6H_6O = C_6H_5.OH$.

—*Phenyl alcohol, Phenic acid, Carboic acid, Coal-tar creosote.*—This compound is produced: 1. By the action of nitrous acid on aniline.

2. By the dry distillation of salicylic (ortho-oxybenzoic) acid. It may be conveniently prepared by heating crystallized salicylic acid strongly and quickly in a glass retort, either alone or mixed with pounded glass or quicklime. Phenol then passes over into the receiver, and crystallizes almost to the last drop.

3. Phenol is produced in the dry distillation of coal, and forms the chief constituent of the acid portion of coal-tar oil; this is the source from which it is most frequently obtained. Crude coal-tar oil is agitated with a mixture of slaked lime and water, the whole being left for a considerable time; the aqueous liquid separated from the undissolved oil is decomposed by hydrochloric acid, and the oily product thus obtained is purified by cautious distillation, the first third only being collected. Or the coal-tar oil is subjected to distillation in a retort furnished with a thermometer, and the portion which passes over between the temperature of 150° and 200° C. (302° – 392° F.) is collected apart. This product is then mixed with a hot, strong solution of caustic potash, and left to stand, whereby a whitish, somewhat crystalline, pasty mass is obtained, which, by the action of water, is resolved into a light oily liquid, and a dense alkaline solution. The latter is withdrawn by a siphon, decomposed by hydrochloric acid, and the separated oil purified by contact with calcium chloride, and redistillation. Lastly, it is exposed to a low temperature, and the crystals formed are drained from the mother-liquid, and carefully preserved from the air.

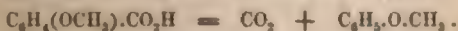
Pure phenol crystallizes in long, colorless, prismatic needles, having a specific gravity of 1.066, melting at 40° – 41° C. (104° – 105.8° F.), and boiling at 181.5° C. (258.7° F.): the commercial product forms a crystalline mass, which turns reddish in a short time, and in contact with moist air deliquesces to a brown liquid. Phenol has a penetrating odor, a strong burning taste, and attacks the skin of the lips. It is poisonous, exerts an antiseptic action, and has been successfully used by Mr. Crookes for

destroying the infection of cattle-plague. It dissolves in about 15 parts of water at ordinary temperatures, very easily in alcohol and ether. Sulphur and iodine dissolve in it; nitric acid, chlorine, and bromine attack it with energy, forming substitution-products, all of which are of acid character. With strong sulphuric acid, it forms phenolsulphonic acid, $C_6H_5(OH).SO_3H$. The aqueous solution is colored violet by ferric chloride, and stains a deal shaving of a fine blue color. With bromine-water, even when very dilute, it forms a white precipitate of tribromophenol.

On adding phenol to nitric acid containing nitrous acid, or to a solution of potassium nitrite (6 per cent.) in strong sulphuric acid, a brown color is produced, changing to green, and ultimately to a fine blue (Liebermann's reaction). Fine colors are produced in like manner with other phenols, mono- and poly-atomic: also by phenols in presence of sulphuric acid with diazo- and nitroso-compounds.

PHENATES.—Phenol dissolves in alkalis, forming salts which are difficult to obtain in definite form. *Potassium phenate*, C_6H_5KO , obtained by heating phenol with potassium, or with solid potassium hydroxide, crystallizes in slender white needles. On heating this potassium-compound with iodide of methyl, ethyl, or amyl, ethers are produced—viz., methyl phenate or anisol, $C_6H_5OC_2H_5$; ethyl phenate or phenetol, $C_6H_5OC_2H_5$, and amyl phenate or phenamylol, $C_6H_5OC_5H_{11}$. These bodies resemble the mixed ethers of the ordinary alcohols (p. 552) in composition and mode of formation, but differ greatly from them in their behavior with sulphuric and nitric acids, with which, in fact, they behave just like phenol itself, forming substitution-products possessing acid properties.

Methyl Phenate or Anisol, $C_7H_{10}O = C_6H_5.O.CH_3$, is also produced, with evolution of carbon dioxide, by distilling methyl-salicylic acid or anisic (methyl-paraoxybenzoic) acid with baryta:



Anisol is a colorless, very mobile liquid, having a pleasant aromatic odor, a density of 0.991 at 15° C. (59° F.), and boiling without decomposition at 152° C. (305.6° F.). It dissolves completely in strong sulphuric acid, forming methyl-phenol-sulphonic or sulphanisolic acid,

$C_6H_5(CH_3) \begin{matrix} \text{OH} \\ \text{SO}_3H \end{matrix}$.—With bromine it forms three substitution-products—viz., $C_6H_4Br.O.CH_3$, a liquid boiling at 223° C. (433.4° F.); $C_6H_3Br_2.O.CH_3$, which crystallizes in rhombic tables, melts at 59° C. (138.2° F.), and boils at 272° C. (521.6° F.); and $C_6H_2Br_3.O.CH_3$, which melts at 87° C. (188.6° F.), and is sublimable. By the further action of bromine, tetrabromoquinone or bromanil, $C_6Br_4O_2$, is produced. Fuming nitric acid acts strongly on anisol, forming the three nitranisols, $C_7H_7(NO_2)O$, $C_7H_6(NO_2)_2O$, and $C_7H_5(NO_2)_3O$, which when treated with reducing agents yield the corresponding nitranisidines, $C_7H_5(NH_2)O$, etc.

Ethyl Phenate or Phenetol, $C_8H_{10}O.C_2H_5$, obtained from phenol, and from ethylsalicylic acid, is an aromatic liquid, boiling at 172° C. (341.6° F.).—Amyl Phenate, or Phenamylol boils at 225° C. (437° F.).

Ethene Phenate, $C_7H_7(OC_2H_5)_2$, produced by the action of ethene bromide on potassium phenate, crystallizes in laminæ melting at 95° C. (203° F.).

Phenyl Phenate, Phenyl Oxide, or Phenolic Ether, $C_{11}H_{10}O = (C_6H_5)_2O$, formed, together with phenyl benzoate, by the dry

distillation of cupric benzoate, and by heating diazobenzene sulphate with phenol, crystallizes in long needles, melts at 28°C . (82.4°F .), and boils at 246°C . (474.6°F .); dissolves easily in alcohol and ether.

Thiophenol or Phenyl Hydrosulphide, $\text{C}_6\text{H}_5\text{SH}$, formed by the action of P_2S_5 on phenol, and by that of nascent hydrogen (zinc and sulphuric acid) on phenyl-sulphochloride, is a colorless, mobile, fetid liquid, having a density of 1.078 at 14°C . (57.2°F .), and boiling at 168°C . (334.4°F .). It is insoluble in water, but dissolves easily in alcohol and ether, and the alcoholic solution is precipitated by silver, lead, and mercury salts, yielding compounds analogous to the mercaptides. The mercury-compound, $(\text{C}_6\text{H}_5\text{S})_2\text{Hg}$, crystallizes from alcohol in shining needles.

Phenyl Sulphide, $(\text{C}_6\text{H}_5)_2\text{S}$, produced by the dry distillation of sodium benzene-sulphonate, and, together with the hydrosulphide, by the action of P_2S_5 on phenol, is a colorless liquid, having an alliaceous odor, a density of 1.12, and boiling at 292°C . (557.6°F .). Nitric acid oxidizes it to phenyl sulphoxide (sulphobenzide) $(\text{C}_6\text{H}_5)_2\text{SO}_2$.

Phenyl Disulphide, $(\text{C}_6\text{H}_5)_2\text{S}_2$, is formed by oxidizing thiophenol with dilute nitric acid, and by the action of iodine on the aqueous solution of potassium-thiophenol:



It crystallizes from alcohol in shining needles melting at 60°C . (140°F .); is oxidized by nitric acid to benzenesulphonic acid, and reduced by nascent hydrogen to thiophenol.

Halogen Derivatives of Phenol.

Chlorophenols.—The three monochlorophenols, $\text{C}_6\text{H}_4\text{Cl.OH}$, *ortho*-, *meta*-, and *para*-, are formed from the corresponding chloranilines (p. 835), by the diazo-reaction. The *ortho*- and *para*-compounds are also produced by passing chlorine into warm phenol, and may be separated by fractional distillation. (1 : 2) *Chlorophenol* is a colorless liquid, boiling at $175^{\circ}\text{--}176^{\circ}\text{C}$. ($347^{\circ}\text{--}348.8^{\circ}\text{F}$.), solidifying at -12°C . (10.4°F .); converted by fusion with potash into pyrocatechin. (1 : 3) *Chlorophenol*, from (1 : 3) chloraniline, is a liquid boiling at 214°C . (417.2°F .). (1 : 4) *Chlorophenol* crystallizes in colorless prisms, which gradually turn red, melts at 37°C . (98.6°F .), boils at 217°C . (422.6°F .); is converted by fusion with potash into hydroquinone. All the three chlorophenols have a very pungent and persistent odor.

Dichlorophenol, $\text{C}_6\text{H}_3\text{Cl}_2\text{OH}$, probably $\text{C}_6\text{H}_3\text{Cl.OH.Cl.H}$, obtained by dry distillation of dichlorosalicylic acid, melts at 43°C . (109.4°F .), and boils at 209°C . (408.2°F .).—**Trichlorophenol**, $\text{C}_6\text{H}_2\text{Cl}_3\text{OH}$ (1 : 3 : 5, OH), the chief product of the action of chlorine on phenol, melts at 68°C . (154.4°F .), and boils at 244°C . (471.2°F .).—**Pentachlorophenol**, $\text{C}_6\text{Cl}_5\text{OH}$, obtained by the action of chlorine on phenol, in presence of antimonious chloride, melts at 187°C . (368.6°F .).

Bromophenols.—The three monobromophenols, $\text{C}_6\text{H}_4\text{Br.OH}$, are obtained from the three corresponding bromanilines; the 1 : 2 and 1 : 4 modifications also, by passing bromine vapor into phenol, and by the action of bromine on a solution of phenol in glacial acetic acid. The *ortho*- and *meta*-

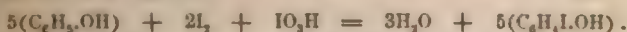
modifications are liquid.—*Pyrobromophenol* forms large crystals; melts at 54° C. (147.2° F.); boils at 236° C. (456.8° F.); and is converted, by the action of phosphorus pentabromide, into *paradibromobenzene*.

Orthobromophenol, $C_6H_4Br_2.OH$ (probably 1 : 2 : 4, OH in 1), obtained by bromination of phenol, melts at 40° C. (104° F.).

Tribromophenol, $C_6H_3Br_3.OH$ (1 : 3 : 5, OH), precipitated by bromine-water from the aqueous solution of phenol, crystallizes from alcohol in silky needles, melting at 95° C. (203° F.). By PBr_3 it is converted into *tribromobenzene*, melting at 98° C. (208.4° F.) (p. 824); by nitric acid into *picric acid*.

Pentabromophenol, $C_6Br_5.OH$, melts at 225° C. (437° F.).

Iodophenols.—The three moniodophenols, $C_6H_4I.OH$, are formed, together with tri iodophenol, by treating phenol with iodine and iodic acid in presence of free alkali:



On supersaturating the liquid with hydrochloric acid, and distilling the precipitated oil with steam, a liquid moniodophenol (1 : 2) passes over first, then a solid (1 : 3), and finally, tri-iodophenol; and the residue contains a considerable quantity of the latter, which may be extracted by alcohol. The third moniodophenol (1 : 4), which is easily soluble in water, is found partly in the aqueous solution from which the crude iodophenol has been precipitated, partly in the aqueous distillate, and partly in the alcoholic solution from which the tri-iodophenol has crystallized.

(1 : 2) Iodophenol, produced also from (1 : 2) amidophenol, and by distillation of *iodosalicylic acid*, is a liquid which does not solidify at -23° C. (-9.4° F.). It is easily decomposed, with separation of iodine, by chlorine and by nitric acid. By fusion with potash it yields *pyrocatechin*. (1 : 3) Iodophenol, produced also from *metaiodaniline*, is somewhat sparingly soluble in water, crystallizes from alcohol in six-sided tables melting at 89° C. (192.2° F.); is not decomposed either by chlorine or by nitric acid. By fusion with potash it yields *resorcin*. (1 : 4) Iodophenol, obtained also from *para-iodaniline*, is very soluble in water, crystallizes in shining needles melting at 64° – 66° C. (147.2° – 150.8° F.); is decomposed by nitric acid, but not by chlorine; converted by fusion with potash at 100° into *hydroquinone*.

Nitrosophenol, $C_6H_4(NO).OH$ (1 : 4).—This compound is formed : 1. By the action of nitrous acid on phenol :



2. As a sodium salt, by heating *nitrosodimethylaniline* (p. 838) with dilute soda-lye :

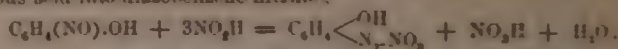


Pure hydrochloride of *nitrosodimethylaniline* is added to a boiling dilute solution of caustic soda; the *dimethylaniline* is distilled off; and the residue, acidified with dilute sulphuric acid, is shaken up with ether.

Nitrosophenol crystallizes from hot water in slender colorless needles, which soon turn brown; from ether in large brown laminae. It dissolves with light green color in water, alcohol, and ether; easily also in dilute soda-lye, forming a sodium-salt, which, on addition of strong caustic soda, separates in red needles containing $C_6H_4(NO).ONa + 2H_2O$. Salts of the

heavy metals added to this solution throw down amorphous dark-colored precipitates.

Nitrosophenol melts when heated, and decomposes with a slight explosion at 120° – 130° C. (248° – 266° F.). By strong nitric acid it is converted into paranitrophenol; by tin and hydrochloric acid into paramitrophenol; by nitrous acid into diazobenzene nitrates:



With aniline acetate it yields diazoxybenzene, $\text{C}_6\text{H}_4(\text{OH})\cdot\text{N}_2\cdot\text{C}_6\text{H}_5$.

On adding strong sulphuric acid to nitrosophenol dissolved in phenol the solution assumes a dark-red color, changing, on addition of potash, to a fine blue.

Nitrophenols.

These compounds, which are all of acid character, are easily formed by direct nitration of phenol.

Mononitrophenols, $\text{C}_6\text{H}_4(\text{NO}_2)\text{OH}$, (1:2) and (1:4), are obtained by gradually adding 1 part of phenol to 2 parts of nitric acid (sp. gr. 1.44), dissolved in 4 parts of water. They may be separated by distillation with water, as only the ortho-compound volatilizes with the steam. The same compounds are produced by heating (1:2) and (1:4) nitrobenzenes in sealed tubes with alcoholic ammonia. The (1:4) and (1:3) compounds may be prepared by boiling the diazonitrobenzene nitrates from (1:4) and (1:3) nitroaniline with water; the (1:4) compound also by heating paranitraniline with very strong solution of caustic soda.

(1:2), commonly called *volatile nitrophenol*, crystallizes in large yellow prisms; dissolves sparingly in water, easily in alcohol, and volatizes easily with vapor of water; melts at 45° C. (113° F.), and boils at 216° C. (417.2° F.); converted by PCl_5 into (1:2) chloronitrobenzene. Its sodium salt, $\text{C}_6\text{H}_4(\text{NO}_2)\text{ONa}$, crystallizes in dark red anhydrous prisms, and the methylic ether, $\text{C}_6\text{H}_4(\text{NO}_2)\text{OCH}_3$, formed from it by the action of methyl iodide, melts at 9° C. (48.2° F.), and boils at 265° C. (509° F.).

(1:3) Nitrophenol forms colorless needles, moderately soluble in water, melting at 96° C. (204.8° F.).

(1:4) Nitrophenol forms long, colorless needles, melting at 112° C. (230° F.), converted by PCl_5 into (1:4) chloronitrobenzene. Its methylic ether melts at 48° C. (118.4° F.), boils at 268° C. (509° F.), and is converted by heating with ammonia into (1:4) nitrandine.

Dinitrophenol, $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH}$ (1:2:4—OH in 1), is formed by the action of strong nitric acid on phenol and on *o*- and *p*-nitrophenol; also by boiling the corresponding dinitrochlorides or dinitro-bromides (p. 831) with alkalis. Colorless plates, melting at 114° C. (237.2° F.).

The consecutive modification (1:2:6—OH in 1), formed, together with the preceding from (1:2) nitrophenol, crystallizes in needles melting at 63° – 64° C. (145.4° – 147.2° F.).

Both these compounds are converted by further nitration into pure acid.

Two other dinitrophenols, formed from (1:3) nitrophenol, the one melting at 104° C. (219.2° F.), the other at 141° C. (285.8° F.), are converted by further nitration into boric acid.

Trinitrophenols, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$.—Two of these compounds are known. (1) *Picric acid*, 1:2:4:6 (OH in 1), also called *resorcinic acid*, is formed by nitration of phenol and of 1:2:4 and 1:2:6 dinitrophenol. It is also one of the ultimate products of the action of nitro-

aid upon indigo and numerous other substances, as silk, wool, several dyes, especially that of *Xanthorrhoea hastilis* (yellow gum of Botany Bay), olein and some of its derivatives, coumarin, etc. It is most economically prepared from phenol. One part of that substance is gradually added to strong nitric acid slightly warmed, and when the first violent reaction has subsided, three parts of fuming nitric acid are added, and the liquid is stirred till nitrous fumes are no longer evolved. The resinous mass thus reduced is boiled with water; the resulting picric acid is converted into sodium-salt; and the solution mixed with sodium carbonate, which throws down the sodium picrate in crystals.

Picric acid crystallizes in yellow shining prisms or laminæ, having an intensely bitter taste. It melts at 122.5°C. (252.5°F.), sublimes when cautiously heated. It dissolves sparingly in cold water, more easily in hot water, still more in alcohol. It stains the skin deep yellow, and is used as a yellow dye for wool and silk. It is a strong acid, forming well-crystallized yellow salts, which detonate violently when heated, some of them also by percussion. The potassium salt, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OK}$, crystallizes in long needles very slightly soluble in water. The sodium, ammonium, and strontium salts are easily soluble in water.

Methyl picrate, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCH}_3$, formed by nitration of anisol (p. 863), crystallizes in tables, which melt at 60°C. (140°F.) and sublime. Ethyl picrate forms colorless needles, which turn brown in the air, and melt at 173°C. (341.3°F.).

Picrates of Hydrocarbons.—Picric acid affords characteristic reactions for the detection of certain hydrocarbons. For this purpose, it is convenient to use an alcoholic solution of the acid saturated at $20^{\circ}\text{--}30^{\circ}\text{C.}$ ($68^{\circ}\text{--}86^{\circ}\text{F.}$), and either—(1) add the hydrocarbon to the cold-saturated alcoholic solution; or (2) mix the picric acid solution with a hot alcoholic solution of the hydrocarbon; or (3) dissolve the hydrocarbon, with aid of heat, in the picric acid solution. The following combine under these circumstances with picric acid: *Naphthalene* is the only solid hydrocarbon whose cold-saturated alcoholic solution is precipitated by picric acid. The compound forms delicate stellate groups of yellow needles, easily soluble in alcohol. *Resene*, treated by method 2 or 3, forms similar needles of an orange-yellow color. *Anthracene* also forms ruby-colored needles still more soluble than the preceding; the red alcoholic solution is decolorized by addition of a little more alcohol. Other hydrocarbons contained in crude anthracene exhibit the same reaction, which appears to be peculiar to anthracene and its homologues. They may be distinguished from one another by the appearance of the precipitates under the microscope.

Picric acid is converted by PtCl_5 into trinitrochlorobenzene, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{Cl}$, which is reconverted into picric acid by boiling with water. Picric acid distilled with calcium hypochlorite, or a mixture of potassium chlorate and hydrochloric acid, yields chloropicrin, $\text{C}(\text{NO}_2)_3\text{Cl}$; and with calcium hypobromite, bromopicrin, $\text{C}(\text{NO}_2)_3\text{Br}$, (p. 527).

Isopicric acid, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, formed by the action of fuming nitric acid on metanitrophenol, crystallizes from hot water or from nitric acid in light yellow prisms, melting at 174°C. (345.2°F.). It stains the skin yellow.

Picrocyamic, or *Isopurpuric acid*, $\text{C}_6\text{H}_2\text{N}_3\text{O}_6$, not known in the free state, is formed, as a potassium salt, $\text{C}_6\text{H}_2\text{N}_3\text{O}_6\text{K}$, by dropping a hot solution of picric acid (1 part in 9 of water) into a solution of potassium cyanide (2 parts CNK in 4 of water) heated to 60°C. (140°F.). This salt crystallizes in brown-red scales, having a green metallic lustre, sparingly soluble in cold water, dissolving in hot water and in alcohol with deep-red color (test for hydrocyanic acid and metallic cyanides). Detonates strongly when heated.

The dinitrophenols treated with potassium cyanide yield similar derivatives.

Nitrohaloid derivatives of phenol, $C_6H_5Cl(NO_2)_2.OH$, etc., are produced by the action of halogen elements on the nitrophenols.

Amidophenols.

These compounds are formed by the action of reducing agents on the nitrophenols, the di- and tri-nitrophenols being partially reduced by basic ammonium sulphide, completely by tin and hydrochloric acid. The entrance of the NH_2 group into the molecule considerably weakens the acid character of the compound, and when it replaces the whole of the nitro-groups, the compound becomes basic.

Monamidophenols, $C_6H_5(NH_2).OH$.—The *ortho*- and *para*-compounds are formed by reduction of the corresponding nitro- or azo-compounds, best with tin and hydrochloric acid: the *p*-compound also by distillation of amidosalicylic acid.—(1:2) amidophenol forms colourless rhombic scales; (1:4) colorless needles, which soon turn brown. They are slightly soluble in cold water, more easily in alcohol, and form red crystallized salts with acids: *o*-melts at $170^\circ C.$ ($338^\circ F.$), *p*-, with decomposition, at $184^\circ C.$ ($363.2^\circ F.$).

Amidonitrophenol or Picramic acid, $C_6H_3(NH_2)(NO_2)_2.OH$.—The ammonium salt of this acid, formed by passing hydrogen sulphide into an alcoholic solution of ammonium picrate, crystallizes in red needles and is decomposed by acetic acid, yielding the free acid, which also forms red needles melting at $165^\circ C.$ ($329^\circ F.$).

Tri-amidophenol, $C_6H_2(NH_2)_3.OH$, is a triacid base not known in the free state. Its *hydrochloride*, $C_6H_2(NH_2)_3.OH.3HCl$, obtained by the action of iodine and phosphorus on a hot saturated solution of picric acid, forms easily soluble colorless needles.—The *hydrochloride*, $C_6H_2(NH_2)_3.OH.3HCl$, obtained by decomposing picric acid with tin and hydrochloric acid, and treating the resulting stannochloride, which separates on cooling, with hydrogen sulphide, crystallizes in needles easily soluble in water, sparingly in strong hydrochloric acid. From these salts the base cannot be separated without decomposition. The solution of the hydrochloride mixed with ferric chloride acquires a deep-blue color, and if concentrated deposits the hydrochloride of **amido-diimidophenol**,

$C_6H_2(OH) \begin{pmatrix} NH_2 \\ NH \\ NH \end{pmatrix}$, in yellow-brown needles, having a blue shimmer to reflected light, and dissolving in water with a fine blue color.

Diazophenol (para).—The *nitrate*, $C_6H_4 \begin{pmatrix} OH \\ N=N \end{pmatrix} NO_2$, is formed together with *o*- and *p*-nitrophenol, by passing nitrous acid into an ethereal solution of phenol or nitrosophenol cooled with ice. It crystallizes in light-brown needles. The other salts of this base, which also crystallize well, are obtained by passing nitrous acid into the solutions of the corresponding salts of *p*-amidophenol. The salts of *ortho*-imidophenol are obtained in like manner. All these salts are analogous in their reactions to the diazobenzene salts.

Phenol-sulphonic acids.

Phenol dissolves easily in strong sulphuric acid, forming *ortho*- and *para*-phenolsulphonic acid, $C_6H_4(OH).SO_3H$. At ordinary temperatures, the *ortho*-acid is almost the only product, but it easily changes into the *para*-acid when heated. The two acids may be separated by fractional crystallization of their potassium salts, the *p*-salt separating out first in elongated, hexagonal tables, which are anhydrous. The mother-liquors yield the *o*-salt in long colorless spicules, containing $2H_2O$. Most of the other salts of the *p*-acid are less soluble than the corresponding *o*-salts. The two acids are not known in the free state. The sodium salt of the *p*-acid, heated with MnO_2 and sulphuric acid, yields quinine. Treated with PCl_5 , it yields *p*-chlorophenol and *p*-dichlorobenzene. The *o*-acid fused with potash yields pyrocatechin; the *p*-acid, by molecular transformation, yields resorcin (see DIATOMIC PHENOLS).

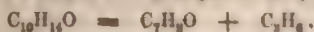
Metaphenolsulphonic acid is formed as a potassium salt by heating potassium benzene-metadisulphonate dissolved in the smallest possible quantity of water, with two or three times its weight of potassium hydroxide for a considerable time to 170° – 180° C. (338° – 356° F.). The greater part of the potassium sulphate formed at the same time having been removed by crystallization, the metaphenolsulphonate may be extracted from the mother-liquor by alcohol. This salt crystallizes from water in groups of easily soluble efflorescent scales containing 1 mol. H_2O . The free acid forms concentric groups of very soluble needles. Ferric chloride colors the solutions of the three acids violet.

Phenoldisulphonic acid, $C_6H_3(OH)(SO_3H)_2$, is formed by heating phenol or *o*- or *p*-phenolsulphonic acid with excess of strong sulphuric acid, whence it has the structure 1 : 2 : 4 (OH in 1); also by the action of sulphuric acid on diazobenzene sulphate. The solutions of the acid and its salts are colored dark red by ferric chloride.

Phenoltrisulphonic acid, $C_6H_2(OH)(SO_3H)_3$ (1 : 3 : 5, OH), formed by the action of strong sulphuric acid or phosphoric anhydride on phenol, crystallizes in thick prisms containing $3\frac{1}{2}H_2O$.

Cresols, $C_7H_8O = C_6H_4 \begin{smallmatrix} CH_3 \\ \diagup \\ OH \end{smallmatrix}$.—*Tolyl alcohols*.—*Para*- and *ortho*-cresol occur in coal- and wood-tar, together with phenol, and may be separated from the latter by fractional distillation; but they cannot easily be separated one from the other. They are obtained in the pure state by fusing the potassium salts of the corresponding toluenesulphonic acids, $C_6H_4(CH_3)(SO_3K)$, with potash, or from the corresponding toluidines by the diazo-reaction (p. 554). They are converted into toluene by heating with zinc-dust, and into the corresponding oxytoluic or cresotic acids, $C_6H_3(CH_3)(OH)(CO_2H)$, by the action of sodium and carbon dioxide.

Orthocresol is likewise obtained, together with propene, by heating carvacrol (cymophenol), $C_{10}H_{14}O$, with phosphoric anhydride:



It is a colorless crystalline mass, melting at 31° – 31.5° C. (87.8° – 88.7° F.), boiling at 185° – 186° C. (365° – 366.8° F.); colored blue by ferric chloride. By prolonged heating with potassium hydroxide it is converted into salicylic acid.

Metacresol, prepared from thymol, $C_{10}H_{14}O$, in the same manner as *o*-cresol from carvacrol, is a colorless liquid which smells like phenol, boils at

201° C. (393.8° F.), remains liquid at the temperature of a mixture of solid carbon dioxide and ether, and is converted by fusion with potash into oxybenzoic acid. Its ethylic ether is an oil boiling at 190° C. (374° F.).

Paracresol forms colorless prisms smelling like phenol, melting at 36° C. (96.8° F.), and boiling at 198° C. (388.4° F.). It dissolves sparingly in water, forming a solution which is colored blue by ferric chloride. By fusion with potash, paracresol is converted into paraoxybenzoic acid. Its ethylic ether is an aromatic liquid boiling at 188° C. (374.4° F.). The *meta*-ethylic ether boils at 174° C. (345.2° F.), and is oxidized by chromic acid to methyl-paraoxybenzoic (anisic) acid, $C_6H_4(OCH_3)(CO_2H)$. The *acetic ether*, $C_6H_4O.C_2H_5O$, is a liquid boiling at 208°–211° C. (406.4°–411.8° F.).

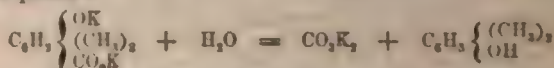
Nitro-cresols.—Several of these compounds are obtained by nitration of paracresol.— $C_6H_3(NO_2)_3O$ crystallizes in yellow needles like picric acid.— $C_6H_6(NO_2)_3O$, obtained also by the action of nitrous acid on paraluidine, is a dye-stuff, known as *Victoria yellow*; it forms yellow crystals, melting at 84° C. (183.2° F.), less soluble in water than picric acid.

Thiocresols, or Toly Hydrosulphides, $C_6H_4\begin{smallmatrix} CH_3 \\ | \\ SH \end{smallmatrix}$, are produced from the three toluenesulphonic acids by reducing the corresponding chlorides, $C_6H_4(CH_3)(SO_2Cl)$, with zinc and hydrochloric acid. (*Ortho*-, shining laminae, melting at 15° C. (59° F.), boiling at 188° C. (370.4° F.). *Meta*-, liquid, not solidifying at –10° C. (14° F.). *Para*-, large laminae, melting at 43° C. (109.4° F.), boiling at 188° C. (370.4° F.).

Eight-carbon Phenols, $C_8H_{10}O$.—This formula includes two metameric phenols, viz.:

| | | |
|-----------------|-----------|--------------------|
| Dimethyl-phenol | : : : : : | $C_6H_3(CH_3)_2OH$ |
| Ethyl-phenol | | $C_6H_4(C_2H_5)OH$ |

Two Dimethyl-phenols or Xylenols are produced by fusing the potassium-salt of xylenesulphonic acid, $C_6H_3SO_3K$, with potassium hydroxide. On decomposing the resulting mass with hydrochloric acid, digesting with ether, and distilling, a liquid passes over at 210° C. (410° F.), which, when exposed to a winter temperature, separates into two isomeric modifications, one crystalline, the other liquid. The solid modification is likewise obtained by fusing the potassium-salt of oxymesitylenic acid with potash:

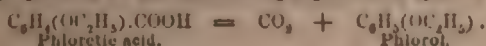


Solid xylénol melts at 75° C. (167° F.) and boils at 216° C. (420.8° F.); the liquid modification boils at 206.5°–208.5° C. (403.7°–407.1° F.).

A xylylic phenol is mentioned by Dr. Hugo Müller as occurring in coal-tar; this is probably also a dimethyl-phenol, inasmuch as products of destructive distillation have hitherto been found to yield only methyl-derivatives of benzene. The portion of aloisol (a product obtained by distilling aloes with lime) which is soluble in potash, has the composition of a xylylic phenol, and is perhaps identical with the preceding. Cresosol, from beech-tar, is a mixture of several phenols and their ethers, and usually consists of phenol, cresol, xylénol, guaiaacol, $C_6H_4(OH)(OCH_3)$, and cresol, $C_6H_4(CH_3)(OH)(OCH_3)$.

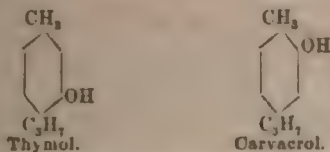
Ethyl-phenol, obtained from ethyl-benzene sulphonic acid, melts at 47° C. (116.6° F.), boils at 211° C. (411.8° F.), and volatilizes even at ordinary temperatures.

Phlorol, an oily liquid obtained by the dry distillation of the barium salt of phloretic or *o*-ethyl-benzoic acid, $C_8H_9O_2$, or $C_8H_4(OC_2H_5).COOH$, is also an ethyl phenol, its formation being represented by the equation:



Phlorol is a colorless, strongly-refracting oil, having a specific gravity of 1.0374 at 12° C. (53.6° F.), and boiling at 226° C. (428° F.). It dissolves in strong sulphuric acid, forming a sulpho-acid which yields a soluble barium salt. With chlorine it forms a substitution-product. It reacts violently with strong nitric acid, forming the compound $C_8H_7(NO_2)_3O$. By sodium and carbon dioxide it is converted into phloretic acid.

Ten-Carbon Phenols, $C_{10}H_{13}.OH$.—Two compounds represented by this formula are known, viz.: thymol and carvacrol. Both are methyl-propyl-phenols, $C_6H_3(CH_3)(C_3H_7)(OH)$, and have the methyl-group in the para-position relatively to the propyl-group; but in thymol the CH_3 -group stands to the OH in the meta-position; in carvacrol in the ortho-position, thus:



Both are resolved by heating with phosphoric anhydride into propene, C_3H_6 , and cresol, thymol yielding meta-, and carvacrol yielding ortho-cresol (p. 869).

Thymol exists, together with cymene, $C_{10}H_{14}$, and thymene, $C_{10}H_{16}$, in the volatile oils of thyme (*Thymus serpyllum*), horse-mint (*Mentha sylvestris*), *Psychotis Afjowan*, an East Indian plant, and *Monarda punctata*, or Oswego tea, a native of North America. It crystallizes in large transparent plates, has a mild odor, a peppery taste, melts at 44° C. (111.2° F.), and boils at 230° C. (446° F.). Its *methyl ether* boils at 205° C. (401° F.), the *ethyl ether* at 220° C. (428° F.).

Thymol treated with *bromine* in sunshine yields pentabromothymol, $C_{10}H_5Br_5O$, and with *chlorine*, $C_{10}H_9Cl_3O$ or $C_{10}H_7Cl_3O$, accordingly as the reaction takes place in the shade or in sunshine; both of these, as well as the bromine-compound, are crystalline.

There are two nitrothymols, $C_{10}H_{17}(NO_2)_2O$ and $C_{10}H_{11}(NO_2)_3O$, obtained by the action of nitric acid on thymolsulphonic acid. Both form potassium salts, which crystallize in yellow or orange-yellow needles.

Carvacrol, *Oxy-cymene*, or *Cymenol*, is obtained by fusing cymen-sulphonic acid, $C_{10}H_{13}.SO_3H$, with potash, and by heating camphor with one-fifth of its weight of iodine; also from the isomeric compound carvol, contained in oil of caraway (*Carum Carui*), by heating with phosphoric acid. It is a thick oil, not solidifying at -25° C. (-13° F.), boiling at 234°-236° C. (451.4°-455° F.).

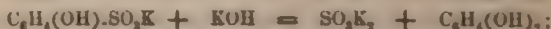
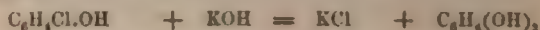
Thymol and carvacrol distilled with phosphoric anhydride yield two isomeric thiophenols, $C_{10}H_{11}.SH$, both of which are non-solidifying liquids. Thymol boils at 230°-231° C. (446°-447.8° F.); thiocymenol at 235° C. (455° F.).

Diatomic Phenols, $C_6H_{2n-4}(OH)_n$.

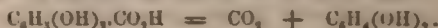
There are seven known compounds included in this formula, viz.:

| | |
|------------------------------------|--------------------------|
| Pyrocatechin—Resorcin—Hydroquinone | . $C_6H_4(OH)_2$ |
| Orcin—Homo-pyrocatechin | . $C_6H_3(CH_3)(OH)_2$ |
| Beta-orcin—Hydrophlorone | . $C_6H_3(CH_3)_2(OH)_2$ |

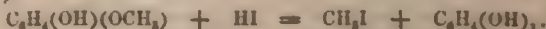
These compounds are formed by the action of melting potash on the monohaloid derivatives of the monatomic phenols, and on the phenolsulphonic acids:



also on resins; and by the dry distillation of aromatic dioxyacids—such as oxysalicylic acid, $C_6H_3(OH)_2.CO_2H$, with lime or baryta:



Pyrocatechin, $C_6H_4(OH)_2$ (1 : 2), also called *Oxyphenic acid*, is formed: 1. By fusing orthochlor- or orth-iodophenol with potash. 2. By the dry distillation of oxysalicylic or of protocatechuic acid, $C_7H_5O_4$. 3. By dry distillation of catechin (the juice of *Mimosa catechu*), from which it was first obtained; also from morintannic acid (the yellow coloring matter of *Morus tinctoria*); and of wood, whence it is found in wood-vinegar. 4. By heating its methylic ether (guaiacol) with hydriodic acid to $200^\circ C$. ($392^\circ F$.).



This reaction affords the best method of preparing it.

Pyrocatechin crystallizes in short-square prisms; sublimes even at ordinary temperatures, in shining laminae; melts at $104^\circ C$. ($219.2^\circ F$.), and boils at $245.5^\circ C$. ($473.9^\circ F$.). It dissolves easily in water, alcohol, and ether. The aqueous solution mixed with ferric chloride assumes a dark-green color, changing to violet on addition of a small quantity of ammonia, acid sodium carbonate, or tartaric acid. Pyrocatechin reduces silver nitrate at ordinary temperatures, an ammoniacal solution of copper with the aid of heat. Nitric acid acts violently upon it, forming oxalic acid and a small quantity of a yellow nitro-compound. With acetyl chloride and benzoyl chloride it forms the compounds $C_6H_4(O.C_2H_5O)_2$ and $C_6H_4(O.C_6H_5O)_2$, both of which are crystalline. Its aqueous solution forms, with lead acetate, a white precipitate, $C_6H_4O_3Pb$.

Methyl-pyrocatechin or **Guaiacol**, $C_7H_8O_2 = C_6H_4 \begin{smallmatrix} \text{OCH}_3 \\ \text{OH} \end{smallmatrix}$, is one of the constituents of beech-tar creosote (p. 870), and may be separated therefrom by fractional distillation. It is produced by heating pyrocatechin with potassium hydroxide and potassium methylsulphate to $180^\circ C$. ($356^\circ F$.); by heating methyl-pyrocatechuic acid with calcium hydrate: $C_7H_5(CH_3)O_4 = CO_2 + C_6H_4(CH_3)O_3$; and by dry distillation of guaiac resin.

Guaiacol is a colorless liquid, having a specific gravity of 1.117, and boiling at $200^\circ C$. ($392^\circ F$.); slightly soluble in water, easily in alcohol, ether, acetic acid, and alkalis. It forms crystalline salts with the alkalis and alkaline earths, and its alkaline solutions reduce the salts of gold, silver, and copper. By heating with hydriodic acid or fusion with potash, it is resolved into pyrocatechin and methyl iodide or methyl alcohol.

Dimethyl-pyrocatechin, $C_6H_4(O.CH_3)_2$, formed by heating the potassium-derivative of methyl-pyrocatechin with methyl iodide, is a liquid boiling at $205^\circ C.$ ($401^\circ F.$).

Resorcin, $C_6H_4(OH)_2$ (1 : 3), is formed by the action of melting potash on the para-modifications of chlorophenol, iodophenol, chloro-, and bromo-benzenesulphonic acids, phenolsulphonic and benzenedisulphonic acids; also on some compounds not belonging to the para-series. It appears, indeed, to be the most stable of the three diatomic phenols, and is accordingly produced by molecular transposition, especially at high temperatures, in some cases when an ortho- or para-compound might be expected to result. Resorcin is also formed by the action of melting potash on umbelliferone, and on various resins and gum-resins, as galbanum, saffetida, gum ammoniacum, sagapenum, and acarcoid resin. It is most easily prepared by the dry distillation of extract of Brazil wood.

Resorcin is very soluble in water, alcohol, and ether, and crystallizes from very concentrated solutions, in prisms belonging to the trimetric system, colorless at first, but afterwards becoming reddish. It melts at $110^\circ C.$ ($230^\circ F.$), and boils at $271^\circ C.$ ($519.8^\circ F.$), distilling almost without residue. Its aqueous solution is colored violet by ferric chloride, is not precipitated by lead acetate, and reduces silver nitrate only at the boiling heat, except in presence of ammonia, in which case the reduction takes place in the cold. These characters distinguish resorcin from pyrocatechin. A very delicate test for resorcin is its conversion into fluorescein (q. r.) by heating with phthalic anhydride. Bromine-water added to the aqueous solution throws down the tribromo-compound, $C_6H_2Br_3(OH)_2$. Resorcin also forms a triacetyl-compound, $C_6H_3(C_2H_3O)(O.C_2H_3O)_3$, and two benzoyl-derivatives, $C_6H_2(O.C_2H_3O)_2$ and $C_6H_3(C_2H_3O)(O.C_2H_3O)_2$.

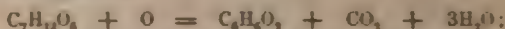
Nitro-resorcins.—*Di-nitroresorcin*, $C_6H_2(NO_2)_2(OH)_2$, formed by adding potassium nitrite to a very dilute solution of resorcin mixed with acetic acid, crystallizes with molecules of water in yellowish-gray or brown laminae, which detonate when heated to $115^\circ C.$ ($239^\circ F.$).

Trinitroresorcin, *Oxyptic*, or *Styphnic acid*, $C_6H(NO_2)_3(OH)_2$, is produced by the action of cold nitric acid on several gum-resins (galbanum, sagapenum, gum ammoniacum), and on many vegetable extracts (Sapan-wood, Brazil-wood, etc.); also by heating meta-nitrophenol with strong nitric acid. It crystallizes in large yellow hexagonal prisms or laminae, sparingly soluble in water, melting at $175^\circ C.$ ($347^\circ F.$), and subliming when cautiously heated, exploding when quickly heated. With ferrous sulphate and lime-water, it exhibits at first a green color, which afterwards disappears (distinction from picric acid, which is thereby colored blood-red). Trinitroresorcin is a strong bibasic acid, forming well-crystallized salts, which detonate violently when heated.

Tri-amido-resorcin, $C_6H(NH_2)_3(OH)_2$.—The hydrochloride of this base, $C_6H_3N_3O_2.3HCl + H_2O$, produced by the action of tin and hydrochloric acid on trinitroresorcin, forms large yellowish, easily soluble crystals. The solution of the stannous-chloride (the immediate product of the reaction) is colored dark-red by ferric chloride, or by exposure to the air, and deposits on standing red needles, consisting of the hydrochloride of amidodiamido-resorcin, $C_6H(OH)_2(NH_2)<\begin{smallmatrix} NH \\ NH \end{smallmatrix}>.HCl$. Ammonia added to the solution of this salt separates the free base in slender needles, having a green metallic lustre.

Hydroquinone, $C_6H_4(OH)_2$ (1 : 4), is formed by fusing para-iodophenol with potash to $180^\circ C.$ ($356^\circ F.$); by dry distillation of oxy-

salicylic and of quinic acid, and by heating the aqueous solution of the latter with lead peroxide :

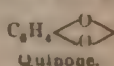
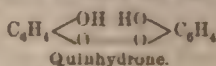
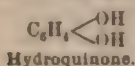


also from arbutin (see GLUCOSIDES), by boiling with dilute sulphuric acid, or by the action of emulsin :



It is most easily prepared from quinone by reduction with sulphurous acid, $\text{C}_6\text{H}_4\text{O}_2 + \text{H}_2 = \text{C}_6\text{H}_6\text{O}_2$. Gaseous sulphur dioxide is passed into an aqueous solution of quinone, till the liquid, which at first assumes a brown color from formation of quinhydrone, becomes colorless. The solution is then evaporated down, and the hydroquinone extracted by ether.

Hydroquinone crystallizes from water in colorless rhombic prisms, melting at 165°C . (335.2°F .), subliming when carefully heated, decomposing when suddenly heated. It dissolves in 17 parts of water at 15°C . (59°F .), easily in alcohol and ether. It unites with hydrogen sulphide and sulphur dioxide, forming crystalline compounds which are decomposed by water. Its aqueous solution is turned red-brown by ammonia, and is not precipitated by lead acetate except in presence of ammonia. Oxidizing agents convert hydroquinone first into quinhydrone, then into quinone:



Substitution-products of hydroquinone are obtained, not directly from hydroquinone, but from the corresponding derivatives of quinone or of arbutin.

Chlorhydroquinones are produced by reduction of chloroquinones with sulphurous acid. $\text{C}_6\text{H}_3\text{Cl}_2\text{O}_2$ melts at 158°C . (316.4°F .), $\text{C}_6\text{H}_2\text{Cl}_3\text{O}_2$ at 134°C . (273.2°F .), $\text{C}_6\text{HCl}_4\text{O}_2$ above 200°C . (392°F .).

Dinitrohydroquinone, $\text{C}_6\text{H}_3(\text{NO}_2)_2(\text{OH})_2$, obtained by boiling dinitro-arbutin with dilute sulphuric acid, forms golden-yellow laminæ; its aqueous solution is colored dark blue by alkalis.

Dichlorhydroquinone-disulphonic acid, $\text{C}_6\text{Cl}_2 \left\{ \begin{array}{c} (\text{OH})_2 \\ (\text{SO}_3\text{H})_2 \end{array} \right.$, is formed by heating tetrachloroquinone with a dilute solution of acid sodium sulphite, tetrachlorhydroquinone being produced in the first instance, and two of its chlorine-atoms then replaced by the groups SO_3H . The aqueous solution of this acid is colored indigo-blue by ferric chloride. A solution of its potassium salt, containing free potash, oxidizes quickly on exposure to the air, and is converted into yellow potassium euthiochrome, $\text{C}_6(\text{OH})_2 \left\{ \begin{array}{c} \text{O}_2 \\ (\text{SO}_3\text{K})_2 \end{array} \right.$.

Quinone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$, is produced by the oxidizing action of manganese dioxide and sulphuric acid, or of dilute chromic acid, on numerous benzene-derivatives (*a. g.*, phenylenediamine, amidophenol, amidobenzene-sulphonic acid), especially those belonging to the para-series; also by distilling various vegetable extracts with MnO_2 and sulphuric acid. It is most easily prepared by gently heating quinic acid (1 part) with manganese dioxide (2 parts) and sulphuric acid (1 part diluted with $\frac{1}{2}$ part water).

Quinone crystallizes in golden-yellow prisms, melts at 116°C . (240.8°F .), and sublimes, even at ordinary temperatures, in shining needles. It has a pungent tear-exciting odor, distils easily with aqueous vapor, and dissolves sparingly in cold water, easily in hot water, also in alcohol and ether. By reduction with sulphurous acid, or with zinc and hydrochloric acid, it is converted, first into quinhydrone, then into hydroquinone. Phosphorus pentachloride converts it into para-dichlorobenzene.

Chloroquinones are formed by the action of chlorine on quinone, and by distilling quinic acid with MnO_2 and hydrochloric acid. $\text{C}_6\text{H}_3\text{Cl}_2\text{O}_2$ forms yellow needles, $\text{C}_6\text{H}_2\text{Cl}_2\text{O}_2$, produced also by the action of hypochlorous anhydride, Cl_2O , on benzene, and by heating trichlorophenol with nitric acid, forms large yellow prisms, melting at 120°C . (248°F .). $\text{C}_6\text{HCl}_3\text{O}_2$, obtained also by the action of chromyl chloride, CrO_2Cl_2 , on benzene, crystallizes in large laminae melting at 166°C . (330.8°F .).

Tetrachloroquinone or *Chloranil*, $\text{C}_6\text{Cl}_4\text{O}_2$, is formed, together with $\text{C}_6\text{HCl}_3\text{O}_2$, from many benzene-derivatives (aniline, phenol, isatin, etc.), by the action of chlorine, or of potassium chlorate and hydrochloric acid. It is best prepared by gradually adding a mixture of 1 part crystallized phenol, and 4 parts potassium chlorate to hydrochloric acid diluted with an equal volume of water, and slowly heating the liquid. Red crystals then separate, which, on further addition of potassium chlorate, are converted into a yellow mixture of tri- and tetra-chloroquinone. To separate these compounds, they are converted by sulphurous acid into the corresponding chlorohydroquinones ($\text{C}_6\text{H}_2\text{Cl}_4\text{O}_2$ is insoluble in water), which are then re-converted into the chloroquinones by oxidation.

Chloranil forms golden-yellow shining laminae, insoluble in water, soluble in hot alcohol and in ether, subliming at about 150°C . (302°F .); converted by PCl_5 into perchlorobenzene.

Chloranil dissolves with purple-red color in dilute potash-lye, forming the potassium salt of chloranilic acid, $\text{C}_6\text{Cl}_2\text{O}_2(\text{OK})_2 + \text{H}_2\text{O}$, which crystallizes in dark red needles, sparingly soluble in water. Acids decompose it, separating chloranilic acid, $\text{C}_6\text{Cl}_2\text{O}_2(\text{OH})_2 + \text{H}_2\text{O}$, in reddish shining scales. Chloranil is converted by aqueous ammonia into chloranilamide, $\text{C}_6\text{Cl}_2\text{O}_2(\text{NH}_2)_2$, and chloranilamic acid, $\text{C}_6\text{Cl}_2(\text{NH}_2)\text{O}_2(\text{OH})$.

Bromoquinones, analogous to the chloroquinones, are obtained by similar reactions. *Bromanil*, $\text{C}_6\text{Br}_4\text{O}_2$, is most readily prepared by heating phenol (1 part) with bromine (10 parts), iodine (3 parts), and water, to 100°C . Golden-yellow laminae sparingly soluble in carbon sulphide.

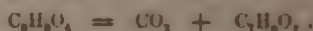
Quinhydrone, $\text{C}_{12}\text{H}_{10}\text{O}_4 = \text{C}_6\text{H}_6\text{O}_2 \cdot \text{C}_6\text{H}_4\text{O}_2 = \begin{matrix} \text{C}_6\text{H}_4(\text{OH})-\text{O} \\ | \\ \text{C}_6\text{H}_4(\text{OH})-\text{O} \end{matrix}$, is formed

by treating quinone in aqueous solution with a quantity of sulphurous acid not sufficient for complete reduction; also by incomplete oxidation of hydroquinone, and by mixing the aqueous solutions of quinone and hydroquinone. It crystallizes in flat prisms, having a splendid golden-green metallic lustre like that of the wing-cases of the rose-beetle, and sublimes in green laminae. It is fusible, has but little odor, dissolves freely in hot water with a brown color, in alcohol and ether with green color. It is resolved, by boiling with water, into quinone which distils over, and hydroquinone; and is converted, by oxidation into quinone, by reduction into hydroquinone.

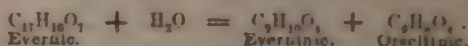
Phenoquinone, $\text{C}_8\text{H}_6 \begin{matrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{matrix} \text{C}_6\text{H}_5$, is produced by careful oxidation of phenol with chromic acid, and (together with quinhydrone and hydroquinone) by mixing the aqueous solutions of quinone and phenol. It forms red, very volatile needles, melting at 71°C . (159.9°F .), soluble

in water, more easily in alcohol and ether. It is colored blue by potash, green by baryta or ammonia.

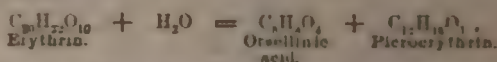
Diatomic Phenols. $C_6H_2O_4 = C_6H_2(CH_2)_2(OH)_2$.—Orcin exists ready formed in all the lichens (*Leccanora tartarea*, *Roccella tinctoria*, *Pezizaria arcana*, etc.) which are used for the preparation of archil and kermes, and is the general product of the decomposition of certain acids extracted from these lichens (orsellinic acid, erythric acid, etc.) under the influence of heat or of alkalis. Orsellinic acid, $C_{11}H_{10}O_7$, when boiled with baryta-water, splits up into carbon dioxide and orcin:



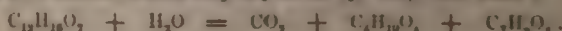
Kvernin acid is resolved by the same treatment into everninic and orsellinic acids:



Erythric acid (erythrin) is resolved, in like manner, into orsellinic acid and picroerythrin:



the orsellinic acid being further resolved, as above, into CO_2 and orcin, and the picroerythrin into CO_2 , erythrite (p. 616), and orcin:



To prepare orcin in quantity, one of the lichens above mentioned is boiled with milk of lime, the liquor filtered and evaporated to one-fourth the lime precipitated by carbonic acid; the filtrate evaporated nearly to dryness on the water-bath; the residue boiled several times with benzene, the orcin extracted from the benzene solution by agitation with water, and the aqueous solution evaporated.

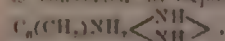
Orcin may also be prepared by the action of melting potash on extract of aloes, and on the potassium-salt of chlorotoluene-sulphonic acid.

Orcin crystallizes in colorless six-sided prisms containing $C_6H_2O_4 \cdot H_2O$. It has a sweet taste, dissolves readily in water, alcohol, and ether, melts at $58^\circ C.$ ($136.4^\circ F.$), gives off its water of crystallization at $80^\circ C.$ ($176^\circ F.$), and boils at $290^\circ C.$ ($554^\circ F.$). Its aqueous solution is precipitated by lead acetate, colored blue-violet by ferric chloride, and exhibits with hypochlorites a transient dark-violet coloration.

The hydroxyl-groups in orcin may be replaced by acid and by alcoholic radicals: the diethylic ether, $C_6H_2(OC_2H_5)_2O_2$, boils at $240^\circ-250^\circ C.$ ($464^\circ-482^\circ F.$).

Tribromorcin, $C_6Br_3(CH_2)_2(OH)_2$, is precipitated by bromine-water from the aqueous solution of orcin.

Trinitro-orcin, $C_6(NO_2)_3(CH_2)_2(OH)_2$, produced by dissolving orcin in a well-cooled mixture of strong nitric and sulphuric acid, forms long yellow needles, which melt at $162^\circ C.$ ($323.6^\circ F.$), and react very much like trinitroresorcin. By the action of tin and hydrochloric acid it is reduced to *triamido-orcin*, $C_6(NH_2)_3(CH_2)_2(OH)_2$, which forms colorless crystals, and is converted by exposure to the air into crystals of *amidobenzotriazene*.



Orcin unites with dry ammonia forming a crystalline compound, $C_6H_2O_4 \cdot NH_3$; and when a solution of orcin containing ammonia is exposed to the

air, it absorbs oxygen, acquires a dark-red or purple color, and gives with acetic acid a deep-red pulverulent precipitate of orcein, $C_7H_7NO_3$, formed according to the equation:



Orcein unites with metallic oxides, forming red lakes. It is the chief constituent of the dyestuffs known as archil, cudbear, French purple, and litmus. The last-mentioned substance, which is extensively used for the preparation of test-papers, is prepared from *Rocella tinctoria* or *Lecanora tartarea*, by macerating the lichen in solution of ammonium carbonate, exposing the liquid to the air for 20 to 40 days, and thickening the coloring matter thus obtained with chalk or gypsum.

Isorcin, $C_6H_3(CH_3)(OH)_2$, obtained from toluidine-disulphonic acid, forms colorless needles, melts at $87^\circ C.$ ($188.6^\circ F.$), and boils at $260^\circ C.$ ($500^\circ F.$).

Homopyrocatechin, $C_7H_8O_2 = C_6H_3(CH_3)(OH)_2$, which has not been obtained in the crystalline state, is produced by the action of hydriodic acid on creosol, $C_8H_{10}O_2 = C_7H_6 \begin{smallmatrix} OH \\ | \\ (CH_3) \end{smallmatrix}$, which is its methylic ether. Creosol is one of the constituents of beech-tar (p. 870), and is formed together with guaiacol, by the dry distillation of guaiac resin. It is a colorless liquid, very much like guaiacol, boils at $219^\circ C.$ ($426.2^\circ F.$), and reduces silver nitrate when heated with it. Its alcoholic solution is colored dark-green by ferric chloride.

Hydrotoluquinone, $C_8H_8(CH_3)(OH)_2$, and *Toluquinone*, $C_8H_6(CH_3)_2O_2$, are not known; but di- and tri-chlorotoluquinone, $C_8H_5Cl_2(CH_3)_2O_2$ and $C_8H_4Cl_3(CH_3)_2(OH)_2$, are formed by the action of hydrochloric acid and potassium chlorate on cresol, just as the six-carbon chloroquinones are obtained from phenol. The trichloro-compound forms yellow laminar crystals, and is converted by heating with aqueous sulphurous acid into trichloro-hydrotoluquinone, $C_8H_5Cl_3(CH_3)(OH)_2$, which crystallizes in colorless needles.


Diatomic Phenols, $C_9H_{10}O_2 = C_9H_8(OH)_2$.—*Hydrophlorone* is obtained by the action of sulphurous acid on phlorone, or xyloquinone, $C_9H_8O_2$, a compound obtained by distilling coal-tar oil or beech-tar creosote, boiling above $210^\circ C.$ ($410^\circ F.$) with MnO_2 and sulphuric acid. It forms colorless laminae, having a mother-of-pearl lustre, fusible, sublimable, easily soluble in water, alcohol, and ether. Oxidizing agents convert it into phlorone, $C_9H_8O_2$, which forms yellow volatile needles.

Beta-orcin is obtained by dry distillation of usnic acid and other acids occurring in lichens, e. g., $C_9H_{10}O_4$ (evermic acid) $= C_9H_{10}O_2 + (CO)_2$. Colorless crystals, easily soluble in hot water, melting at $109^\circ C.$ ($228.2^\circ F.$). The aqueous solution turns red when mixed with ammonia and exposed to the air, and is colored dark red by bleaching powder.

Veratrol, obtained by distillation of veratric acid, $C_9H_{10}O_4$, with baryta, is an oil solidifying at $15^\circ C.$ ($59^\circ F.$), and boiling at 202° – $205^\circ C.$ (395.6° – $401^\circ F.$).

Thymohydroquinone, $C_{10}H_{12}(OH)_2 = C_6H_2(CH_3)(C_3H_7)(OH)_2$, the only known diatomic phenol containing 10 atoms of carbon, is produced by the action of sulphurous acid on thymoquinone, and crystallizes in lustrous, shining, four-sided prisms, melting at $139.5^\circ C.$ ($283.1^\circ F.$), and subliming without decomposition; converted by oxidation into thymoxyl-

none. Its methylic ether is a constituent of the volatile oil of *Artemisia montana*.

Thymoquinone, $C_{10}H_{12}$  (*thymol*), is produced by distilling thymol and carvacrol with MnO_2 and sulphuric acid. It crystallizes in yellow tables, melts at $45.5^\circ C.$ ($113.9^\circ F.$), and boils at $200^\circ C.$ ($392^\circ F.$).

Triatomic Phenols, $C_6H_3(OH)_3$.

Pyrogallol or Pyrogallie Acid, is produced by the action of heat on gallic (dioxysalicylic) acid: $C_7H_5O_5 = CO_2 + C_6H_3O_3$; also, together with gallic acid, by the action of hot caustic potash on di-iodosalicylic acid, $C_7H_3I_2O_5$. It is conveniently prepared by heating a dried aqueous extract of gall-nuts to $180^\circ-185^\circ C.$ ($350^\circ-365^\circ F.$) in an iron pot covered with a paper cap; it then sublimates and condenses on the cap in long flattened prisms.

Pyrogallol is soluble in water, alcohol, and ether; it melts at $115^\circ C.$ ($239^\circ F.$), boils at $210^\circ C.$ ($410^\circ F.$), and decomposes at $250^\circ C.$ ($482^\circ F.$), giving off water, and leaving a residue of metagallic acid, $C_6H_3O_4$. Pyrogallol dissolves in caustic potash or soda, forming a solution which quickly absorbs oxygen from the air, and turns black; this solution forms a very convenient reagent for the endiometric analysis of air (p. 150). With solutions of ferrous salts, it produces a black-blue color; with ferric salts a red color. Pyrogallol quickly reduces gold, silver, and mercury from their salts, and forms, with lead acetate, a white precipitate, $C_6H_3O_3PbO$.

With bromine pyrogallol forms a tribromo-derivative, $C_6Br_3(OH)_3$; with acetyl chloride it yields a triacetyl-derivative, $C_6H_3(OC_2H_3O)_3$, forming crystals slightly soluble in water.

Phloroglucin, $C_6H_3O_3$. Phlorizin, or Phloridzin, $C_{23}H_{34}O_{10}$, a crystalline substance found in the root-bark of the apple, pear, plum, and cherry trees, is resolved by boiling with dilute acids into glucose and phloretin, $C_{15}H_{14}O_5$:



and phloretin heated with aqueous potash is resolved into phloretic acid and phloroglucin:



Phloroglucin crystallizes in large colorless prisms containing $2H_2O$; effloresces on exposure to the air; gives off all its crystallization-water at $100^\circ C.$; melts at $230^\circ C.$ ($446^\circ F.$), and sublimates without decomposition. It has a sweet taste, and dissolves easily in water, alcohol, and ether. Its aqueous solution is precipitated by lead acetate, and colored dark violet by ferric chloride.

Phloroglucin is converted by chlorine into dichloroacetic acid; with bromine and with nitric acid it forms tri-substitution derivatives; with acetyl chloride and benzoyl chloride it yields the ethers $C_6H_3 \left\{ \begin{smallmatrix} (OH)_2 \\ (OC_2H_3O) \end{smallmatrix} \right.$, and $C_6H_3 \left\{ \begin{smallmatrix} (OH)_2 \\ (OC_7H_7O) \end{smallmatrix} \right.$, both of which are crystalline. Its dibutyryl ether, $C_6H_3 \left\{ \begin{smallmatrix} OH \\ (OC_4H_9O) \end{smallmatrix} \right.$, called *filic acid*, occurs in the root of the male fern

(*Aspidium Filix mas*) as a crystalline substance, which is resolved by fusion with potash into phloroglucin and butyric acid.

With ammonia phloroglucin forms the basic compound, phloramine, $C_6H_3 \begin{Bmatrix} (OH)_2 \\ NH_2 \end{Bmatrix}$, which forms crystalline salts with acids.

Appendix to the Phenols—PHENOL-DYES.

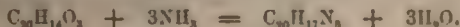
Aurin or Rosolic Acid, $C_{20}H_{14}O_3$ (or $C_{20}H_{16}O_3$?).—This compound, also called *Corallin*, is a red coloring matter, obtained by heating phenol with oxalic and sulphuric acid, the oxalic acid being then resolved into CO, CO_2 , and H_2O , and the CO reacting with the phenol, as shown by the equation:



To obtain a pure product, the mixture of sulphuric acid and phenol must be heated on a water-bath, and the oxalic acid added gradually, waiting each time till the evolution of gas ceases, and not using sufficient oxalic acid to attack all the phenol. The aurin thus obtained has exactly the composition $C_{20}H_{14}O_3$.*

A commercial dye-stuff, known as aurin, corallin, or peonin, which gives a fine yellow-red color to wool and silk, is prepared in a similar manner. It is a mixture of several substances, but may be purified by treatment with aqueous ammonia, which dissolves the extraneous matters, leaving a residue of nearly pure aurin.

The same compound is obtained by the action of nitrous acid on rosaniline (p. 848); and it is reconverted into that base by heating with ammonia in aqueous or alcoholic solution.



From this it would appear that the formula of rosaniline should be $C_{20}H_{17}N_3$, whereas, according to Hofmann's analysis, its composition is $C_{20}H_{19}N_3$. Further investigation is therefore required to clear up this discrepancy.†

Aurin crystallizes from alcohol in red prisms, having a green metallic lustre. It is insoluble in water, but soluble in alcohol, strong hydrochloric acid, and glacial acetic acid. It unites with sulphurous anhydride, forming garnet-red crystals, $(C_{20}H_{14}O_3)_2SO_2 + 5\frac{1}{2}H_2O$, and forms crystalline compounds with bisulphites of alkali-metal, e.g., $C_{20}H_{14}O_3 \cdot NaHSO_3$. Bromine added to its acetic acid solution throws down the compound $C_{20}H_{16}Br_4O_3$ in shining green laminae.

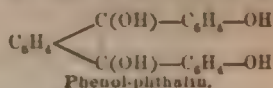
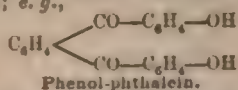
By reduction with zinc-dust in alcoholic solution, aurin is converted into leucaurin, $C_{20}H_{16}O_3$, which crystallizes from alcohol in colorless prisms, and is reconverted into aurin by oxidation. *Triacetyl-leucaurin*, $C_{20}H_{14}(C_2H_3O)_3O_3$, produced by heating leucaurin with acetyl chloride, forms short silky needles, easily soluble in alcohol and in acetic acid.

Phthaleins.—These are compounds formed, with elimination of water, by the combination of phenols with phthalic anhydride, $C_8H_4O_3$, or $C_6H_5 \begin{Bmatrix} (O) \\ (O) \end{Bmatrix} O$. They contain the ketonic group CO, together with the

* Dale and Schorlemmer, Chem. Soc. Journ., 1873, 434; and 1877, vol. II. p. 121.

† Dale and Schorlemmer observe that, in the analysis of organic coloring-matters, the percentage of hydrogen is often found too high.

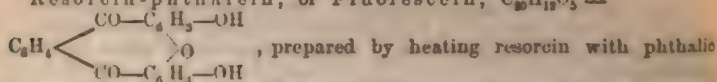
hydroxyl-groups of the phenols, and are consequently intermediate in character between the phenols and ketones. They are all more or less colored, and act as dye-stuffs. By hydrogenation (action of zinc-dust in alkaline solution) they are converted into phthalins, colorless compounds in which the ketonic groups are converted into alcoholic groups, $C(OH)$; e. g.,



By oxidation, the phthalins are reconverted into phthaleins.

Phenol-phthalein, $C_{20}H_{14}O_4$, is prepared by heating 10 parts of phenol with 5 parts of phthalic anhydride and 4 parts of strong sulphuric acid to $120^\circ C.$ ($248^\circ F.$) for about ten hours, exhausting the product with boiling water, dissolving the residue in dilute caustic soda, and precipitating with acetic acid and a little hydrochloric acid. It may be purified by boiling its alcoholic solution with animal charcoal, and precipitating the filtrate with water. It then separates as a white or yellowish-white crystalline powder, or in triclinic crystals, according as the precipitation is effected quickly or slowly. It dissolves in alkalis with fuchsin-red color, and on heating the alkaline solution with zinc-dust, it becomes colorless, from conversion of the phthalein into phenol-phthalin, $C_{20}H_{14}O_4$, which separates on addition of hydrochloric acid, in white prisms. This compound dissolves in strong sulphuric acid, and the solution, mixed with water, deposits an amorphous yellowish substance, $C_{20}H_{14}O_6$, called phenol-phthalidin, which may be reconverted into the phthalin by heating with water to $175^\circ C.$ ($347^\circ F.$). By exposure to the air, or more quickly, by treatment with manganese dioxide, potassium manganate or potassium ferricyanide, it is converted into a compound, $C_{20}H_{14}O_6$, isomeric with phenol-phthalein, which separates in monoclinic crystals.

Resorcin-phthalein, or Fluorescein, $C_{20}H_{12}O_5 =$

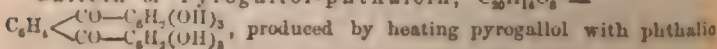


anhydride to $200^\circ C.$ ($392^\circ F.$), forms dark-brown crystals, which dissolve in ammonia, forming a red solution with splendid green fluorescence. On adding bromine to its solution in glacial acetic acid, tetrabromoresorcin-phthalein, or Eosin, gradually separates in crystals, which may be purified by conversion into a potassium-salt and precipitation with an acid. From dilute alcohol it separates in dull, flesh-colored crystals; from absolute alcohol in red crystals containing 1 molecule of alcohol. Its potassium-salt, $C_{20}H_6Br_4O_5K_2$, known in commerce as "soluble eosin," dyes silk of a fine rose-color.

Pyrocatechin-phthalein, $C_{20}H_{12}O_5$, formed by gently heating pyrocatechin with phthalic anhydride and sulphuric acid, dissolves in potash-lye with a fine blue color. Hydroquinone-phthalein, formed in like manner, dissolves in strong sulphuric acid with brick-red color, in alkalis with violet color.

Orcin-phthalein, $C_{27}H_{16}O_5$, forms colorless needles, dissolving in alkalis with dark-red color, without fluorescence.

Gallein or Pyrogallol-phthalein, $C_{20}H_{14}O_6 =$



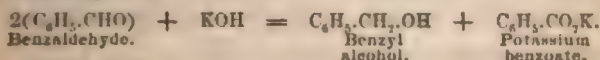
anhydride to 190°–200° C. (374°–392° F.), forms a brown-red powder or small crystals, with green surface-color. It dissolves in alcohol with dark-red, in potash-lye with fine blue color. By zinc-dust, or by zinc and sulphuric acid, it is converted into gallin, $C_{20}H_{18}O_7$, which forms nearly colorless crystals, and is converted by heating to 200° C. (392° F.), with strong sulphuric acid, into cœrulein, $C_{20}H_{10}O_7$, a blue dye-stuff which dissolves in alkalis with green, in aniline with splendid blue color, and is reduced by zinc-dust to cœrulin.

Normal Aromatic Alcohols.

These compounds, formed by substitution of OH for H in the lateral chains of the hydrocarbons homologous with benzene, contain the group CH_2OH , and are therefore primary alcohols, convertible by oxidation into aldehydes and acids containing the same number of carbon-atoms as the alcohols themselves, and producible by methods similar to those which yield the primary alcohols of the fatty series, viz.: (1) From the hydrocarbons by conversion, first into haloid derivatives, such as $C_6H_5.CH_2Cl$, then into acetic ethers, and saponification of the latter with caustic alkalis; e. g.,



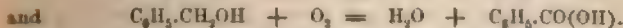
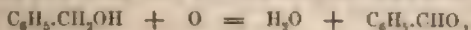
(2) From the aldehydes, by the action of nascent hydrogen, or by heating with alcoholic potash:



Monatomic Alcohols.

Benzyl Alcohol, $C_7H_8O = C_6H_5.CH_2OH$, may be prepared by the methods just mentioned, or by the action of nascent hydrogen on benzoic or hippuric acid. Its benzoic ether, $C_7H_5O_2.C_7H_7$, is one of the constituents of Peru and Tolu balsams.

Benzyl alcohol is a colorless, strongly refracting, oily liquid, having a specific gravity of 1.051 at 14° C. (57.2° F.), and boiling at 207° C. (404.6° F.). It is insoluble in water, but soluble in all proportions in common alcohol, ether, acetic acid, and carbon bisulphide. By oxygen in presence of platinum black, or by nitric acid, it is converted into benzoic aldehyde; by aqueous chromic acid, into benzoic acid:



Strong hydrochloric acid converts it into benzyl chloride, C_7H_7Cl . Distilled with acetic acid and strong sulphuric acid, it is converted into benzyl acetate, $C_6H_5(OC_2H_3O)$, a liquid having an odor of pears, and boiling at 210° C. (410° F.). Benzyl oxalate, $C_7O_4(C_7H_7)_2$, forms shining laminae melting at 80° C. (176° F.).

Alcoholic benzyl ethers are formed by heating benzyl chloride with solutions of potash in the corresponding alcohols. Methyl benzoate, $C_6H_5O.CH_3$, boils at 166° C. (334.4° F.); ethyl benzoate, $C_6H_5O.C_2H_5$, at 185° C. (365° F.). Benzyl-phenylate, $C_6H_7O.C_6H_5$, formed by

heating benzyl chloride with potassium phenate, C_6H_5OK , melts at $35^\circ C$ ($102.2^\circ F.$), boils at $287^\circ C$. ($548.6^\circ F.$). Dibenzyl ether, $(C_6H_5)_2O$, obtained by heating benzyl alcohol with boric oxide [$2C_6H_5(OH) = H_2O = (C_6H_5)_2O$], or by heating benzyl chloride with water to $190^\circ C$. ($374^\circ F.$), is an oil boiling above $300^\circ C$. ($572^\circ F.$).

Chlorobenzyl alcohol (para), $C_6H_4Cl.CH_2OH$, produced by heating para-chlorobenzyl chloride, $C_6H_4Cl.CH_2Cl$, with aqueous ammonia, forms long needles, melts at $66^\circ C$. ($150.8^\circ F.$), and boils without decomposition. Other haloïd benzyl alcohols are formed in a similar manner.

Paranitrobenzyl alcohol, $C_6H_4(NO_2).CH_2OH$, produced by saponification of paranitrobenzyl acetate (obtained by nitration of benzyl acetate), is soluble in hot water, and melts at $93^\circ C$. ($199.4^\circ F.$).

Benzyl hydrosulphide or *Benzyl mercaptan*, $C_6H_5.CH_2SH$, obtained by the action of alcoholic potassium hydrosulphide on benzyl chloride, is a liquid having an alliaceous odor, a specific gravity of 1.058 at $20^\circ C$. ($68^\circ F.$), and boiling at $194^\circ C$. ($381.2^\circ F.$). Its alcoholic solution gives, with metallic salts, precipitates consisting of benzyl-mercaptides, e. g. $(C_6H_5.CH_2S)_2Hg$.

Benzyl sulphide, $(C_6H_5.CH_2)_2S$, formed by the action of potassium monosulphide on benzyl chloride, in alcoholic solution, crystallizes in colorless needles melting at $49^\circ C$. ($120.2^\circ F.$). By oxidation with nitric acid, it is converted into benzyl oxysulphide, $(C_6H_5.CH_2)_2SO$, which is soluble in hot water, and melts at $130^\circ C$. ($266^\circ F.$).

Benzyl disulphide, $(C_6H_5.CH_2)_2S_2$, formed by oxidation of benzyl mercaptan exposed to the air, crystallizes from alcohol in shining scales melting at $66^\circ C$. ($150.8^\circ F.$). Nascent hydrogen converts it into benzyl mercaptan.

All these sulphur compounds of benzyl are decomposed by heat.

Xylol Alcohol,* $C_8H_{10}O = C_6H_5 \begin{smallmatrix} CH_3 \\ | \\ CH_2OH \end{smallmatrix}$.—Of the three isomeric modifications of this alcohol only the para-compound is known. It is obtained from the corresponding aldehyde, and from para-xylol chloride, $C_6H_4(CH_3).CH_2Cl$, by the methods above described. It crystallizes in needles, dissolves sparingly in water, melts at $59^\circ C$. ($138.2^\circ F.$), and boils at $217^\circ C$. ($422.6^\circ F.$). Nitric acid converts it into toluic aldehyde, $C_6H_4(CH_3).CHO$. By heating with hydrochloric acid it is converted into xylol chloride. Its acetic ether boils at $243^\circ C$. ($469.4^\circ F.$). The chloride treated with KHS and K_2S yields the compounds $C_8H_9(SH)$ and $(C_8H_9)_2S$.

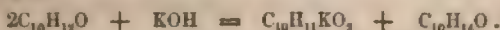
Metamerie with the xylol alcohols are—(1) *Primary phenyl-ethyl alcohol*, $C_6H_5.CH_2.CH_2OH$, formed by the action of sodium amalgam on a solution of alpha toluic (phenyl-acetic) aldehyde, $C_6H_5.CH_2.CO.H$, dissolved in aqueous alcohol. Colorless liquid, boiling at $212^\circ C$. ($413.6^\circ F.$). Specific gravity, 1.0337 at $21^\circ C$. ($69.8^\circ F.$). Converted by gradual oxidation into alpha-toluic acid. Its acetic ether boils at $224^\circ C$. ($435.2^\circ F.$).

(2) *Secondary phenyl-ethyl alcohol*, $C_6H_5.CH(OH).CH_3$, prepared from bromethyl-benzene, $C_6H_5.CHBr.CH_3$ (p. 27), in the same manner as benzyl alcohol from benzyl chloride; and by the action of sodium-amalgam on acetophenone, $C_6H_5.CO.CH_3$. It is a colorless liquid, boiling at $202^\circ C$.— $203^\circ C$. (395.6° — $397.4^\circ F.$), having a density of 1.013, and reconverted by oxidation into acetophenone.

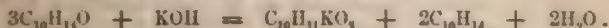
* Generally called tolyl alcohol; but this name is inappropriate. If $C_6H_5.CH_2.CH_2OH$ is to be called tolyl alcohol, then $C_6H_5.CH_2OH$ should by analogy be called not benzyl alcohol, but phenyl alcohol. The true tolyl alcohol is cresol, $C_6H_4 \begin{smallmatrix} CH_3 \\ | \\ OH \end{smallmatrix}$, metamerie with benzyl alcohol, $CH_2 \begin{smallmatrix} CH_3 \\ | \\ OH \end{smallmatrix}$.

Phenyl-propyl Alcohol, $C_9H_{12}O = C_6H_5.CH_2.CH_2.CH_2.OH$, produced by the action of nascent hydrogen on styryl alcohol or cinnamic alcohol, $C_9H_{10}O$, is a liquid boiling at $235^{\circ}C.$ ($455^{\circ}F.$). Secondary phenyl-propyl alcohol, $C_9H_{12}.CH(OH).CH_3$, formed by the action of nascent hydrogen on ethyl-phenyl ketone, is a liquid boiling at 210° – $211^{\circ}C.$ (410° – $411.8^{\circ}F.$).

Cymyl Alcohol, $C_{10}H_{14}O = C_{10}H_{13}(OH) = C_9H_{11}.CH_2OH$, also called *Cumylic Alcohol*.—This alcohol, discovered by Kraut, is produced, together with cumic acid, $C_{10}H_{12}O_2$, by the action of alcoholic potash on cumic aldehyde:



It is a colorless liquid, boiling at $243^{\circ}C.$ ($469.4^{\circ}F.$), insoluble in water, soluble in all proportions in common alcohol and ether. Nitric acid converts it into cumic acid. Boiled with alcoholic potash, it is converted into potassium cumate and cymene:



Hydrochloric acid gas converts it into cymyl chloride, $C_{10}H_{13}Cl$. Metamerie with this compound is:

Benzyl-dimethyl Carbinol, or Phenyl-katabutyl Alcohol,

$O-C \begin{matrix} \nearrow CH_3 \\ \searrow CH_2(C_6H_5) \end{matrix}$, obtained, similarly to tertiary butyl alcohol, by the action of zinc-methyl on phenyl-acetic or α -toluic chloride, $C_6H_5.CH_2.COCl$, crystallizes in long colorless needles, melts at 20° – $22^{\circ}C.$ (68° – $71.6^{\circ}F.$), and boils at 220° – $230^{\circ}C.$ (428° – $446^{\circ}F.$).

Sycoceryl Alcohol, $C_{18}H_{30}O = C_{18}H_{29}(OH) = C_{17}H_{27}.CH_2OH$. This compound, discovered by De La Rue and Müller, is produced by the action of alcoholic soda on sycoceryl acetate (a crystalline substance extracted from the resin of *Ficus rubiginosa*), and purified by precipitation with water or by crystallization from common alcohol. It forms very thin crystals resembling caffeine, and melting at $90^{\circ}C.$ ($194^{\circ}F.$) to a liquid heavier than water. It is slowly attacked by dilute nitric acid, yielding a crystalline mass apparently consisting of a mixture of sycoceric acid, $C_{18}H_{30}O_2$, and nitrosycoceric acid, $C_{18}H_{27}(NO_2)O_2$. Boiled with dilute aqueous chromic acid, it yields thin prisms, probably of sycoceric aldehyde, $C_{17}H_{28}O$. With acetyl chloride, it forms crystalline sycoceryl acetate:



With benzoic acid it yields, in like manner, sycoceryl benzoate, $C_{18}H_{29}.O.C_6H_5O$, which crystallizes in prisms from solution in benzene or chloroform.

The resin of *Ficus rubiginosa*, an Australian plant, is resolved by treatment with alcohol, into about 73 per cent. of sycoretin, soluble in cold alcohol, 14 per cent. of sycoceryl acetate, soluble in hot alcohol, and 1 per cent. of residue, consisting of caoutchouc, sand, and fragments of bark. Sycoretin is an amorphous white neutral resin, very brittle, and highly electric; it melts in boiling water to a thick liquid which floats on the surface. It dissolves easily in alcohol, ether, chloroform, and oil of turpentine.

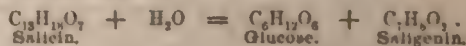
Diatomic Alcohols.

Benzylene Glycol, $C_6H_5.CH(OH)_2$, appears (for reasons already assigned, p. 600), to be incapable of existing, the reactions which might be expected to produce it leading in reality to the production of benzaldehyde, $C_6H_5.CHO$. Its ethers are formed from benzal chloride, $C_6H_5.CHCl_2$ (p. 826) by the action of sodium alcoholates, or of the salts of organic acids. The *dimethylic ether*, $C_6H_5.CH(OCH_3)_2$, boils at $208^\circ C.$ ($406.4^\circ F.$); the *diethylic ether*, $C_6H_5.CH(OC_2H_5)_2$, at $223^\circ C.$ ($431.6^\circ F.$). The *acetic ether*, $C_6H_5.CH(O.C_2H_3O)_2$, is crystalline; melts at $36^\circ C.$ ($96.8^\circ F.$), and boils at $190^\circ C.$ ($374^\circ F.$), being resolved at the same time into benzaldehyde and acetic anhydride.

Xylylene Glycol (para), $C_6H_4 \begin{smallmatrix} \text{CH}_2.OH \\ \text{CH}_2.OH \end{smallmatrix}$, obtained by heating para-xylylene bromide or dibromopara-xylylene, $C_6H_4(CH_2Br)_2$, with water to $170\text{--}180^\circ C.$ ($338\text{--}356^\circ F.$), crystallizes in colorless needles melting at $112\text{--}113^\circ C.$ ($233.6\text{--}235.4^\circ F.$), easily soluble in water, converted by oxidizing agents into terephthalic acid. Its diacetic ether, $C_6H_4(CH_2.OC_2H_3O)_2$, melts at $47^\circ C.$ ($116.6^\circ F.$).

The following compounds have the hydroxyl groups, partly in the principal, partly in the lateral chains, and are therefore both alcohols and phenols.

Saligenin, $C_7H_6O_2 = C_6H_4(OH)-CH_2OH$, or *Ortho-oxylbenzyl alcohol*, is formed by the action of nascent hydrogen on salicylic aldehyde, $C_6H_4(OH).CHO$; and by decomposition of salicin, $C_{13}H_{16}O_7$, (a bitter substance found in willow and poplar bark), under the influence of emulsin or synaptase, the ferment of sweet almonds.



Saligenin forms colorless, nacreous scales, freely soluble in water, alcohol, and ether. It melts at $82^\circ C.$ ($179.6^\circ F.$), and decomposes at about 100° . Dilute acids at boiling heat convert it into saliretin, C_7H_6O , a resinous substance differing from saligenin by the elements of water. The same substance is produced directly from salicin by boiling with dilute acids. Many oxidizing agents, as chromic acid and silver oxide, convert saligenin into salicylic aldehyde and salicylic acid: this shows that it is an ortho-compound. The aqueous solution of saligenin gives a deep indigo-blue color with ferric salts.

Chlorinated derivatives of saligenin, viz., $C_7H_7ClO_2$ and $C_7H_6Cl_2O_2$, are obtained by the action of synaptase on the corresponding chlorosalicin.

Anisyl Alcohol, or **Methyl-paroxybenzyl Alcohol**, $C_8H_{10}O_2 = C_6H_4 \begin{smallmatrix} OCH_3 \\ CH_2.OH \end{smallmatrix}$, is prepared from anisaldehyde (p. 890), in the same manner as benzyl alcohol from benzaldehyde. It crystallizes in colorless shining prisms; has a faint odor and burning taste; melts at $25^\circ C.$ ($77^\circ F.$), and distills undecomposed at $258.8^\circ C.$ ($497.8^\circ F.$). By oxidizing agents it is converted into anisaldehyde and anisic acid; by hydrochloric acid into a volatile chloride, $C_8H_9(OCH_3).CH_2Cl$.

Vanillic, or Methyl-protocatechuic Alcohol, $C_8H_{10}O_3 =$

$C_6H_5 \begin{array}{l} \diagup OCH_3 \\ | OH \\ \diagdown CH_2.OH \end{array}$, obtained by the action of sodium-amalgam on an aqueous solution of vanillin (*q. v.*), forms colorless prismatic crystals, melting at $103-105^\circ C.$ ($217.4-221^\circ F.$), soluble in water and in alcohol.

Piperonylic, or Methene-protocatechuic Alcohol, $C_8H_8O_3 =$

$C_6H_5 \begin{array}{l} \diagup O \\ | \diagdown CH_2 \\ | CH_2.OH \end{array}$, obtained in like manner from piperonal (*q. v.*), forms long colorless prisms, melting at $57^\circ C.$ ($134.6^\circ F.$), sparingly soluble in cold, more easily in hot water, very soluble in alcohol.

A triatomic alcohol called **Stycerin, or Phenyl-glycerin**, $C_9H_{11}O_3 = C_6H_5.CH(OH).CH(OH).CH_2OH$, formed by heating the corresponding dibromhydrin, $C_6H_5.CHBr.CHBr.CH_2OH$, with water to 100° for 24 hours, is a light yellow gummy mass, easily soluble in water and in alcohol. The *dibromhydrin*, obtained by direct combination of bromine with styryl alcohol, forms large colorless shining plates or slender needles, melting at $74^\circ C.$ ($165.2^\circ F.$). The *tribromhydrin*, $C_9H_9Br_3 = C_6H_5.CHBr.CHBr.CH_2Br$, obtained by treating the dibromhydrin with excess of concentrated hydrobromic acid, forms shining needles melting at $124^\circ C.$ ($255.2^\circ F.$).

2. UNSATURATED ALCOHOLS and PHENOLS :

Cinnyl Alcohol, Styryl Alcohol, or Styrene, $C_9H_{10}O = C_6H_5OH$, or $C_6H_5.CH=CH.CH_2OH$, is obtained by heating styracine or cinnyl cinnamate, $C_9H_9(OC_2H_5O)$ (a compound contained in liquid storax and in balsam of Peru), with caustic alkalis. It crystallizes in soft silky needles, having a sweet taste and an odor of hyacinths, melting at $33^\circ C.$ ($91.4^\circ F.$), and volatilizing, without decomposition, at a higher temperature. It is moderately soluble in water, freely in alcohol and ether. By oxidizing agents it is converted into cinnamic aldehyde, C_9H_8O , and cinnamic acid, $C_9H_8O_2$, being related to those compounds in the same manner as ethyl alcohol to acetic aldehyde and acetic acid. With *fuming sulphuric acid* it forms a sulpho-acid, $C_9H_{10}SO_3$, the barium-salt of which is soluble in water. It unites directly with 2 atoms of bromine, forming styeric dibromhydrin, $C_9H_{10}Br_2O$, described above.

Allyl Phenol, or Anol, $C_9H_{10}O = C_6H_4(OH)(C_3H_5)$, formed by fusing *unsaldehyde* (*p.* 890) with potash, crystallizes in shining laminae, melting at $92^\circ C.$ ($197.6^\circ F.$), and decomposing when distilled.

Methyl-allyl Phenol, Anethol, or Anise-camphor, $C_{10}H_{12}O = C_6H_4(OC_2H_5)(C_3H_5)$, is a constituent of the volatile oils of anise, fennel, and tarragon, and separates therefrom on cooling in soft shining scales, melting at $20^\circ C.$ ($68^\circ F.$), and boiling at $225^\circ C.$ ($437^\circ F.$). By oxidation with chromic acid, it is resolved into acetic and anisic acids. On heating it with hydriodic acid, the methyl group is separated, and the mass becomes resinized.

Eugenol, $C_{10}H_{12}O_2 = C_6H_3(OH)(OCH_3)(C_3H_5)$, (*Eugenic, or Caryophyllic acid*), occurs in oil of cloves (from the flowers of *Caryophyllus aromaticus*),

in oil of pimento (from *Myrtus pimenta*), and a few other volatile oils, and may be obtained therefrom by solution in potash, filtration, and precipitation by carbonic acid. It is a colorless, aromatic liquid, of sp. gr. 1.0779 at 0°, boiling at 247.5° C. (477.5° F.), soluble in alcohol. Ferric chloride colors the solution blue. Eugenol, heated with hydrochloric acid, gives off methyl iodide. By fusion with potash it is resolved into acetic acid and protocatechuic acid, $C_8H_7(OH)_2.CO_2H$. These reactions determine its constitution.

Eugenol dissolves in soda-lye, forming sodium-eugenol— $C_8H_7(OH)(ONa)(OCH_3)$, which is converted by methyl iodide into methyl-eugenol— $C_8H_7(C_2H_5)(OCH_3)_2$, which, by oxidation with chromic acid mixture, yields dimethyl-protocatechuic acid, $C_8H_7(OCH_3)_2.CO_2H$. In like manner are formed ethyl-eugenol, propyl-eugenol, etc.

Coniferyl alcohol, $C_{10}H_{12}O_2 = C_6H_5(OH)(OCH_3).C_3H_7OH$, is formed by the decomposition of coniferin (see Glucosides) under the influence of emulsin. It crystallizes in colorless prisms, melting at 74–75° C. (165.2–167° F.); is insoluble in cold water, slightly soluble in hot water, easily in ether and in alkalies. Dilute acids convert it into a resinous polymeric substance. By oxidation with chromic acid mixture it yields vanillin (p. 391).

Cholesterin, $C_{25}H_{41}O$, a product of the animal organism, is homologous with amyl alcohol, and has the characters of a monatomic alcohol. It is found in small quantity in various parts of the animal system, as in the bile, the brain and nerves, and the blood: it forms the chief ingredient of *biliary calculi*, from which it is easily extracted by boiling the powdered gall-stones in strong alcohol, and filtering the solution while hot. On cooling, the cholesterin crystallizes in brilliant colorless plates. It is a fatty substance, insoluble in water, tasteless, and inodorous; it is freely soluble in boiling alcohol and in ether, also in chloroform, and crystallizes from the alcoholic solution in beautiful white laminae having a mother-of-pearl lustre. It melts at 137° C. (278.6° F.), and sublimes at 290° C. (532° F.). On adding a solution of cholesterin in chloroform to strong sulphuric acid, the chloroform becomes purple-red, while the sulphuric acid below it exhibits a greenish-yellow fluorescence: the red chloroform solution evaporated in a porcelain capsule turns blue, green, and finally yellow.

Heated with strong sulphuric acid, it gives up water, and yields a carbonous hydrocarbon, $C_{20}H_{42}$. With nitric acid it yields cholesteric acid, $C_8H_{10}O_3$, together with other products. With chlorine and bromine it forms substitution-products. Heated to 200° C. (392° F.) with acetic, butyric, benzoic, and stearic acids, it forms compound ethers. The *acetic* and *stearic* crystallizes in needles, the former melting at 92° C. (197.6° F.), the latter at 200° C. (392° F.). The *benzoic* forms thick prisms, melting at 125–130° C. (257–266° F.). With PCl_5 , or strong hydrochloric acid, it yields the *chloride*, $C_{25}H_{41}Cl$, which crystallizes in needles, and is converted by ammonia into *cholesteramine*, $C_{25}H_{43}.NH_2$.

Isocholesterin, $C_{26}H_{44}O$, occurs, together with cholesterin, in the grease of sheep's wool, and may be separated by saponifying the fat, heating the mixture of cholesterin and isocholesterin thus obtained with benzoic acid, whereby they are converted into benzoic ethers, and crystallized these compounds from common ether, the cholesteryl benzoate separates in thick tabular crystals, the isocholesteryl benzoate in slender needles, and from the latter the isocholesterin may be obtained by heating with alcoholic potash. It crystallizes from ether or acetone in slender needles, melting at 137–138° C. (278.6–280.2° F.). It does not give any reaction with chloroform and sulphuric acid, but in other respects it reacts like cholesterin. Its benzoic ether melts at 190–191° C. (374–375.8° F.).

AROMATIC ALDEHYDES.

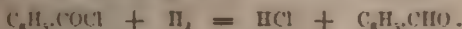
1. ALDEHYDES ANALOGOUS TO MONATOMIC ACIDS.

Four aldehydes are known, belonging to the series $C_6H_{2n-6}O$, analogous to benzoic acid and its homologues, viz.:

| | |
|---------------------|-----------------|
| Benzoic Aldehyde, | C_7H_6O |
| Toluic Aldehyde, | C_8H_8O |
| Cumic Aldehyde, | $C_{10}H_{12}O$ |
| Sycoceryl Aldehyde, | $C_{18}H_{22}O$ |

These aldehydes exhibit the same general reactions as those of the fatty series, and are obtained by similar processes.

Benzoic Aldehyde, Benzaldehyde, or Bitter-almond oil. $C_7H_6O = C_6H_5.CHO = C_7H_5O.H$, is produced—1. By the oxidation of benzyl alcohol. 2. By the action of nascent hydrogen on chloride or cyanide of benzyl:

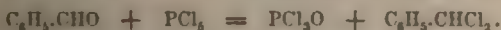


3. By heating benzal chloride, $C_6H_5.CHCl_2$, with water to 130° – 140° C. (265° – 284° F.). 4. By heating benzyl chloride, $C_6H_5.CH_2Cl$, with an aqueous solution of lead nitrate. 5. By the oxidation of amygdalin with nitric acid. 6. By digesting bitter almonds with water for five or six hours at 30° – 40° C. (86° – 104° F.). The synaptase present then acts as a ferment on the amygdalin, converting it into glucose, benzoic aldehyde, and hydrocyanic acid (see GLUCOSIDES).

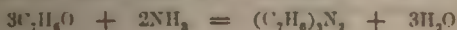
7. Benzoic aldehyde is formed, together with many other products, by the action of a mixture of manganese dioxide and sulphuric acid on albumin, fibrin, casein, and gelatin.

Pure benzoic aldehyde is a thin, colorless liquid, of great refractive power, and peculiar, very agreeable odor; its density is 1.050 at 15° C. (59° F.), and its boiling point 180° C. (356° F.): it is soluble in about 30 parts of water, and miscible in all proportions with alcohol and ether. Exposed to the air, it rapidly absorbs oxygen, and is converted into crystallized benzoic acid. Heated with solid *potassium hydride*, it gives off hydrogen, and yields potassium benzoate. With the *alkaline bisulphites* it forms beautiful crystalline compounds. The vapor of the oil is inflammable, and burns with a bright flame and much smoke.

Benzoic aldehyde, treated with *sodium amalgam*, is converted into benzyl alcohol, C_7H_8O . With *phosphorus pentachloride* it yields benzal chloride, $C_6H_5Cl_2$:



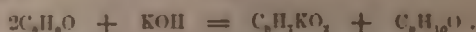
Ammonia converts it into hydrobenzamide, a white crystalline neutral body, which, when boiled with aqueous potash, is converted into an isomeric basic compound called *amarine*:



All the aromatic aldehydes act with ammonia in a similar manner, and are thereby distinguished from the fatty aldehydes.

Amarine and hydrobenzamide yield by dry distillation an isomeric base, $C_8H_8N_2$, called *lophine*, which crystallizes in long, sparingly soluble needles, melting at 290° C. (554° F.), and unites with acids, forming crystalline salts.

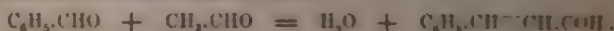
Toluic Aldehyde, $C_8H_8O = C_6H_4 \begin{smallmatrix} \text{CH}_3 \\ \text{CHO} \end{smallmatrix}$ (1 : 4), is produced by distilling a mixture of the calcium-salts of *para*-toluic and formic acid. The only distillate agitated with acid sodium sulphate, forms a crystalline compound, which, when distilled with sodium carbonate, yields the aldehyde, as an oil having a peppery odor, and boiling at $204^\circ C.$ ($399.2^\circ F.$). On exposure to the air, it is gradually converted into *para*-toluic acid, $C_8H_8O_2$. With alcoholic potash it forms potassium *para*-toluate and *para*-xylyl alcohol:



Cumic Aldehyde, $C_{10}H_{12}O = C_6H_4 \begin{smallmatrix} \text{CH}_3 \\ \text{CHO} \end{smallmatrix}$ (1 : 4), exists, together with cymene, $C_{10}H_{14}$, in the essential oil of annin, and in that of water-henlock (*Cicuta virosa*), and may be obtained by agitating either of these oils with acid sodium sulphate, which takes up the cumic aldehyde, but not the cymene, and forms a crystalline compound, from which the aldehyde may be separated by distillation with potash. Cumic aldehyde is a colorless or slightly yellow liquid having a powerful odor, and boiling at $237^\circ C.$ ($458.6^\circ F.$). It is easily oxidized in the air, so that it must be distilled in a current of carbonic acid gas. It is converted into cumic acid, $C_{10}H_{12}O_2$, by oxidation, and by alcoholic potash into potassium cumate and cymyl alcohol, $C_{10}H_{14}O$.

Sycocerylic Aldehyde, $C_{15}H_{24}O$, is produced in thin prisms by oxidizing sycoceryl alcohol with aqueous chromic acid.

Cinnamic Aldehyde, C_9H_8O .—This compound, which is the only known member of the series of aldehydes $C_nH_{2n-10}O$, constitutes the essential part of the volatile oils of cinnamon and cassia, which are obtained from the bark of different trees of the genus *Cinnamomum*, and *Laurea*—viz., oil of cinnamon from Ceylon cinnamon, and oil of cassia from Chinese cinnamon. The aldehyde may be separated from these oils by means of acid potassium sulphite. It is produced artificially by oxidation of styryl alcohol; by dry distillation of a mixture of cinnamic acid formate of calcium, and by saturating a mixture of benzaldehyde and acetaldehyde with hydrochloric acid:



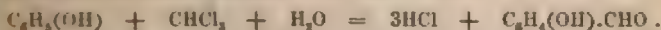
This last reaction is analogous to the formation of crotonic aldehyde by condensation of acetaldehyde (p. 673).

Cinnamic aldehyde is a colorless oil, rather heavier than water. It may be distilled without alteration in a vacuum, or with de-aerated water, but absorbs oxygen quickly on exposure to the air, and passes into cinnamic acid. When fused with potash, it forms potassium cinnamate and gives off hydrogen: $C_9H_8O + KOH = C_9H_7KO_2 + H_2$. Ammonia, NH_3 , converts it into hydrocinnamide: $3C_9H_8O + 2NH_3 = (C_9H_8)_2N_2 + 3H_2O$.

2. ALDEHYDES ANALOGOUS TO DIATOMIC AND MONOBASIC ACIDS.

Salicylic Aldehyde, or **Salicylal**, $C_7H_6O = C_6H_4 \begin{smallmatrix} \text{OH} \\ \text{CHO} \end{smallmatrix}$ (1 : 2).
Orthobenzaldehyde, formerly called *Salicylic Acid*.—This compound occurs

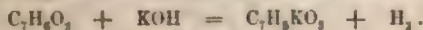
in herbaceous Spiræas, especially in the flowers of meadow-sweet (*Spiræa almaria*). It is formed artificially by oxidizing saligenin, $C_6H_4(OH).CH_2OH$ (p. 884), or its glucosides, salicin and populin (see GLUCOSIDES), and, together with the isomeric para-compound, by the action of chloroform on an alkaline solution of phenol :



This last reaction affords the easiest method of preparing salicylal. Chloroform (3 parts) is gradually added, with agitation, to a solution of phenol (2 parts) and sodium hydroxide (4 parts) in 6-7 parts of water at 50° - 60° C. (122° - 140° F.), in a vessel with reversed condenser; and a quantity of water is added, sufficient to form (after heating to 60° C. [140° F.] for half an hour) a clear red-brown liquid, which is to be kept boiling for two hours, then acidulated and distilled. Salicylal and phenol then pass over, while para-oxybenzaldehyde remains behind. The distillate is shaken with ether, and the salicylic aldehyde is separated from the ethereal solution by agitation with acid sodium sulphite.

Salicylal is a thin, colorless, fragrant oil, acquiring a red tint by exposure to the air. It has a specific gravity of 1.1725 at 15° C. (59° F.), solidifies at -20° C. (-4° F.), boils at 196° C. (384.8° F.), and burns with a bright smoky flame. Water dissolves a perceptible quantity of salicylal, acquiring its fragrant odor, and the property (likewise exhibited by salicylic acid) of producing a deep-violet color with ferric salts. Alcohol and ether dissolve it in all proportions.

Salicylal is oxidized to salicylic acid by boiling with cupric oxide in alkaline solution, partly also by potassium dichromate and sulphuric acid; it likewise reduces silver oxide. When heated with potassium hydroxide it is converted into potassium salicylate, with evolution of hydrogen :



By nascent hydrogen it is converted into saligenin, $C_7H_5O_2$; by ammonia into hydrosalicylamide :



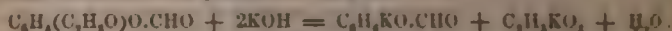
Salicylal is attacked by chlorine and bromine, forming $C_7H_5ClO_2$ and $C_7H_5BrO_2$, both of which are crystalline bodies, having acid properties. With moderately strong nitric acid it forms nitrosalicylal, $C_7H_5(NO_2)O_2$, which is also crystallizable, and forms crystallizable salts. With PCl_5 , at ordinary temperatures, salicylal forms orthoxybenzal chloride, $C_6H_4(OH).CHCl_2$, crystallizing in prisms, and melting at 82° C. (179.6° F.); and when heated with PCl_5 , it yields orthochlorobenzal chloride, $C_6H_4Cl.CHCl_2$, a liquid boiling at 227° - 230° C. (440.6° - 446° F.), and isomeric with parachlorobenzal chloride from toluene (p. 826).

Salicylal dissolves in alkalis, forming crystalline compounds, formerly called *salicylates*. The potassium compound, $C_7H_4(OK).CHO$, forms square plates, easily soluble in water and in alcohol, and decomposing quickly when exposed in the moist state to the air.

Methyl-salicylal, $C_6H_4(OCH_3).CHO$, obtained by the action of methyl iodide on potassium salicylal, is a liquid boiling at 238° C. (460.4° F.). Ethyl-salicylal, prepared in like manner, boils at 248° C. (478.4° F.).

Acetyl-salicylal, $C_6H_4(OC_2H_5).CHO$, metamerie with coumaric acid (*q. c.*), is formed by the action of acetic anhydride on sodium-salicylal at ordinary temperatures: $C_6H_4(ONa).CHO + (C_2H_5O)_2O = C_6H_4(ONa).OC_2H_5 + C_6H_4(OC_2H_5).CHO$. The acetic oxide is added to an equiva-

lent quantity of powdered anhydrous sodium-salicylal suspended in per dry ether, and after the whole has stood for twenty-four hours, the superfluous liquid is filtered off from the sodium acetate, then evaporated, and the crystalline cake which separates on cooling is purified by pressure between bibulous paper, and crystallization from alcohol. Acetosalicylal thus prepared melts at 37°C . (98.6°F .), boils at about 253°C . (477.4°F .), and distills without decomposition. It forms definite compounds with alkaline bisulphites. It is decomposed by alcoholic potash, with formation of potassium acetate and potassium-salicylal:



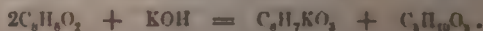
Acetosalicylal likewise unites directly with acetic oxide.

If the product of the action of acetic oxide on salicylal, instead of being treated in the manner above described, be poured into water after a few minutes' boiling, an oily liquid sinks to the bottom, and sodium acetate remains in solution; and on distilling this oil, and collecting apart that which passes over after the temperature has risen to 200°C . (392°F .), a crystalline substance is obtained, having the composition of *acetosalicylal minus one molecule of water*: this substance is identical in every respect with coumarin or coumaric anhydride,* the odoriferous principle of the Tonic bean (see *Coumaric Acid*).

Paraoxybenzaldehyde, $\text{C}_6\text{H}_4(\text{OH}).\text{CHO}$ (1:4), is produced together with salicylic aldehyde, by the action of chloroform on phenol dissolved in caustic soda (p. 889), and may be extracted by ether from the filtered residue of the distillation, and purified by recrystallization from water. It forms stellate groups of slender needles; melts at $115-116^{\circ}\text{C}$. ($239-240.8^{\circ}\text{F}$.); sublimes without decomposition, dissolves sparingly in cold water more readily in hot water, easily in alcohol and ether. Ferric chloride colors its solution dingy violet. It forms easily soluble compounds with alkaline bisulphites.

Anisaldehyde or Methyl-paroxybenzaldehyde, $\text{C}_6\text{H}_4(\text{OCH}_3).\text{CHO}$, isomeric with methyl-salicylal, is formed together with anisic acid by oxidation of anisic alcohol, $\text{C}_6\text{H}_4(\text{OCH}_3).\text{CH}_2\text{OH}$, in contact with platinum, and also by the oxidizing action of dilute nitric acid on the volatile oils of anise, fennel, and tarragon, which contain anethol, $\text{C}_{10}\text{H}_{12}\text{O}$. The product of the oxidation is shaken up with the acid sodium sulphate, and the resulting crystalline compound is decomposed by solution of sodium carbonate.

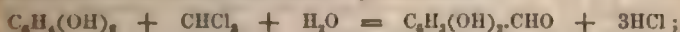
Anisaldehyde is a colorless oil, having an aromatic odor and burning taste, a density of 1.123 at 15°C . (59°F .), and boiling at 248°C . (478.4°F .). It is nearly insoluble in water, but soluble in all proportions in alcohol and ether. It is converted by oxidation into anisic acid, $\text{C}_6\text{H}_4(\text{OCH}_3).\text{CO}_2\text{H}$, by nascent hydrogen into anisic alcohol, $\text{C}_6\text{H}_4(\text{OCH}_3).\text{CH}_2\text{OH}$, and forms crystalline compounds with alkaline bisulphites. Ammonia converts it into anisic diamide, $\text{C}_6\text{H}_4(\text{OCH}_3).\text{CONH}_2$. By alcoholic potash it is decomposed in the same manner as benzoic aldehyde, yielding potassium anisate and anisic alcohol:



* Perkins, Chem. Soc. Journ., 1868, p. 181.

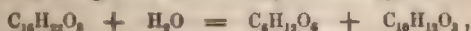
3. ALDEHYDES ANALOGOUS TO MONOBASIC AND TRIATOMIC ACIDS.

Dioxybenzaldehyde or Protocatechuic Aldehyde, $C_7H_6O_3 = C_6H_3(OH)_2CHO$ ($CHO : OH : OH = 1 : 3 : 4$), produced by the action of chloroform on an alkaline solution of pyrocatechin :



also by boiling dichloropiperonal with water, and by heating vanillin or piperonal with dilute hydrochloric acid to $200^\circ C.$ ($392^\circ F.$). Flat shining crystals, melting at $150^\circ C.$ ($302^\circ F.$), easily soluble in water. The aqueous solution is colored deep green by ferric chloride; by fusion with potash, the aldehyde is converted into protocatechuic acid.

Vanillin, $C_8H_8O_3 = C_6H_3(OH)(OCH_3).CHO$, *Methyl-protocatechuic Aldehyde*, is the odoriferous principle of vanilla (the fruit of *Vanilla aromatica*), in which it exists to the amount of about 2 percent. It is produced artificially from coniferin, $C_{16}H_{22}O_6$, a glucoside occurring in the cambial secretion of all coniferous plants, by oxidation with chromic acid mixture; or the coniferin may be resolved by boiling with dilute acids, or by the action of emulsin, into glucose and coniferyl alcohol (p. 886) :



and the coniferyl alcohol oxidized by chromic acid mixture. Vanillin is also produced (similarly to protocatechuic aldehyde) by the action of chloroform on an alkaline solution of guaiacol (methyl pyrocatechin, p. 490).

Vanillin crystallizes in stellate groups of colorless needles, melts at 80° – $81^\circ C.$ (176° – $177.8^\circ F.$), and sublimes when cautiously heated; dissolves sparingly in cold, more freely in hot water, easily in alcohol and ether. It forms crystalline compounds with bases. When boiled with dilute hydrochloric acid, it is resolved into methyl chloride and protocatechuic aldehyde; and when fused with potash, it is converted, by oxidation of the aldehyde-group CHO , and separation of the methyl-group into protocatechuic acid. Bromine converts it into bromovanillin, $C_8H_7BrO_3$, which crystallizes in yellowish laminae melting at $161^\circ C.$ ($321.8^\circ F.$).

Dimethyl-protocatechuic Aldehyde, or **Methyl-vanillin**, $C_8H_8(OCH_3)_2CHO$, and **Ethyl-methyl-protocatechuic Aldehyde**, or **Ethyl-vanillin**, $C_9H_{10}(OCH_3)(OC_2H_5).CHO$, are formed by the action of methyl iodide or ethyl iodide on potassium-vanillin. Both crystallize in colorless prisms, slightly soluble in cold water, somewhat more easily in alcohol and ether. The former melts at 15° – $20^\circ C.$ (59° – $68^\circ F.$), and boils at $285^\circ C.$ ($545^\circ F.$); the latter melts at 64° – $65^\circ C.$ (147.2° – $149^\circ F.$), and easily sublimes.

Piperonal, $C_8H_6O_3 = CH_2 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown O \diagup \end{smallmatrix} C_6H_3-CHO$, *Methene-protocatechuic Aldehyde*, is obtained by distilling a dilute solution of potassium piperate with potassium permanganate, and agitating the distillate with ether. It forms long, colorless, shining crystals, having a very pleasant odor; melts at $37^\circ C.$ ($98.6^\circ F.$), boils at $263^\circ C.$ ($505.4^\circ F.$); dissolves sparingly in cold, more freely in hot water, easily in alcohol and ether; unites with acid sulphites of alkali-metal. Heated with 3 mol. PCl_5 , it yields liquid dichloropiperonal chloride, $C_8H_4Cl_2O_3$, which is resolved by cold water into hydrochloric acid and dichloropiperonal, $C_8H_4Cl_2O_3 = CCl_2 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown O \diagup \end{smallmatrix} C_6H_3-CHO$, and by boiling with water into CO_2 and protocatechuic aldehyde.

4. ALDEHYDES ANALOGOUS TO BISASIC ACIDS.

Phthalic Aldehyde, $C_8H_6O_2 = C_6H_4(CHO)_2$ (1 : 2), is formed by treating phthalyl chloride, $C_8H_4O_2Cl_2$, with zinc and hydrochloric acid, or by dissolving magnesium in a cooled solution of phthalyl chloride, and may be extracted by neutralizing the solution with sodium carbonate and agitating with ether. It crystallizes from hot water in small colorless rhombic tables, melts at 65° , and sublimes when cautiously heated; dissolves sparingly in cold, more readily in boiling water, easily in alcohol and ether.

Terephthalic Aldehyde (1 : 4) is formed by prolonged boiling of tolylene chloride (p. 528) with water (20 parts) and lead nitrate (1 part), and subsequent distillation. Crystallizes in slender needles, melting at 114° – 115° C. (237.2° – 239° F.).

Both these aldehydes dissolve sparingly in cold, more readily in boiling water, easily in alcohol; the ortho-compound is moderately soluble, the para-compound easily soluble in ether. Both form crystalline compounds with acid sodium sulphite.

KETONES.

The aromatic ketones may contain either two aromatic alcohol-radicals (phenyl and its homologues), or one aromatic radicle and one aliphatic radicle (methyl, etc.) belonging to the fatty series. The latter only will be noticed in this place, the former in connection with the diphenyl-compounds.

Phenyl-methyl Ketone or Acetophenone, $C_6H_5.CO.CH_3$, is formed by distilling a mixture of benzoate and acetate of calcium, or by the action of zinc-methyl on benzoyl chloride:



It crystallizes in large laminae melting at 14° C. (57.2° F.), is converted by nascent hydrogen into phenyl-ethyl alcohol (p. 882), and resolved by oxidation with chromic acid into benzoic acid and carbon dioxide.

Phenyl-ethyl Ketone or Propiophenone, $C_6H_5.CO.C_2H_5$, from benzoate and propionate of calcium, and by the action of zinc-ethyl on benzoyl chloride, is a liquid which boils at 208 – 210° C. (406.4° – 410° F.), is converted by nascent hydrogen into secondary phenyl-propyl alcohol, and resolved by chromic acid into benzoic and acetic acids.

Phenyl-propyl Ketone and Phenyl-isopropyl Ketone, $C_6H_5.CO.C_3H_7$, $C_6H_5.CO.C_3H_7$, are formed by distilling a mixture of calcium benzoate and butyrate or isobutyrate respectively. The former boils at 220 – 222° C. (428 – 431.6° F.), and is oxidized by chromic acid to benzoic and propionic acids; the latter boils at 215° C. (419° F.), and is oxidized by chromic acid to benzoic, acetic, and carbonic acids.

Benzyl-methyl Ketone, $C_6H_5.CH_2.CO.CH_3$, formed by distillation of alphetoluate (phenyl-acetate) and acetate of calcium, and by the action of zinc-methyl on alphetol chloride, boils at 214 – 216° C. (417.2 –

420.80° F.), unites with acid sodium sulphite, and is oxidized by chromic acid to benzoic and acetic acids.

Benzyl-ethyl Ketone, $C_6H_5 \cdot CH_2 \cdot CO \cdot C_2H_5$, from alphetoluic chloride with zinc-ethyl, boils at 226° C. (438.8° F.), and is oxidized by chromic acid to benzoic and propionic acids.

AROMATIC ACIDS.

1. MONATOMIC ACIDS, $C_nH_{2n-6}O_2$.

These acids, which bear the same relation to the hydrocarbons homologous with benzene that the fatty acids, $C_nH_{2n}O_2$, bear to the paraffins, C_nH_{2n+2} , are produced by reactions analogous to some of those which yield the fatty acids, viz.:

1. By oxidation of the corresponding aldehydes and alcohols: thus benzoic acid, $C_6H_5O_2$ or $C_6H_5 \cdot COOH$, is formed by oxidation of benzaldehyde, $C_6H_5 \cdot COH$, and of benzyl alcohol, $C_6H_5 \cdot CH_2OH$.

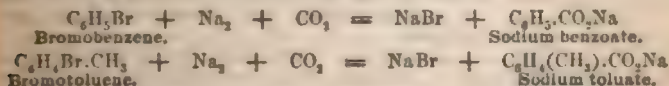
2. By the action of water on the corresponding acid chlorides.

3. By the action of acids or alkalis at the boiling heat on the aromatic nitrils (cyanides of phenyl and its homologues, p. 828):



Benzoic acid and its homologues are likewise obtained by the following processes:

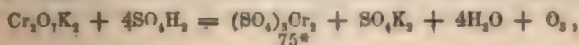
4. By the action of sodium and carbon dioxide on the monobrominated derivatives of benzene and its homologues; e. g.,



5. By oxidation of the hydrocarbons homologous with benzene by means of chromic acid mixture or dilute nitric acid. By chromic acid the lateral chains, CH_3 , $CH_2 \cdot CH_3$, etc., are at once oxidized to CO_2H ; and the hydrocarbons which contain only one lateral chain, $C_6H_5 \cdot CH_3$, $C_6H_5 \cdot C_2H_5$, etc., are all oxidized to benzoic acid, while those which contain two lateral chains are converted into acids containing two carboxyl-groups (di-carbon acids), the xylenes, $C_6H_4(CH_3)_2$, for example, into phthalic acids, $C_6H_4(CO_2H)_2$. With dilute nitric acid, on the other hand, monocarbon acids are produced, at least in the first instance, the xylenes, for example, yielding toluic acids, $C_6H_4(CH_3) \cdot CO_2H$.

For oxidation with chromic acid, 40 grams of potassium dichromate are mixed with 37 grams of strong sulphuric acid diluted with 2 to 3 vol. water; to this mixture 10-20 parts of the hydrocarbon are added, and the whole is boiled for some time in a flask provided with a long upright condensing tube, till all the chromic acid is reduced and the solution has acquired a pure green color. The product is then diluted with water, boiled with solution of sodium carbonate, and the organic acid is precipitated from the filtrate by hydrochloric acid.

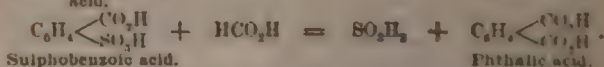
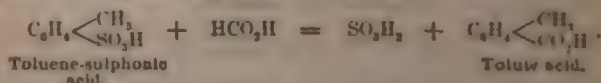
With the proportions above mentioned the reaction takes place according to the equation:



the three atoms of oxygen thus liberated serving for the oxidation of the hydrocarbon.

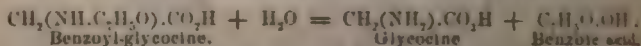
For oxidation with nitric acid, the hydrocarbon is boiled for two or three days with ordinary nitric acid diluted with 3 parts of water in a flask with a vertical condensing tube. To remove the nitro-acids formed at the same time, the crude product is heated with tin and strong hydrochloric acid, whereby the nitro-acids are converted into amido-acids, which dissolve in the hydrochloric acid.

6. By fusing the sulpho-acids of the aromatic hydrocarbons, or the sulpho-aromatic acids, with potassium formate:



The aromatic acids occur, either free or combined, in many resins and balsams and in the animal organism.

Benzoic Acid, $\text{C}_7\text{H}_6\text{O}_2 = \text{C}_6\text{H}_5\text{CO}_2\text{H}$.—This acid, the analogue of benzyl alcohol, is produced by the first four of the general methods above mentioned, and by boiling hippuric acid (benzoyl-glycocine) or the urine of cows or horses, which contains that acid, with strong hydrochloric acid:



This process is applied to the preparation of benzoic acid on the large scale. Benzoic acid is also produced by the oxidation of a great variety of organic bodies, as toluene, cumene, cinnamaldehyde, cinnamic acid, cinnamene, casene, gela tin, etc.



Fig. 176.

Benzoic acid exists ready-formed in several balsams and gum-resins, especially in gum-benzoin, which exudes from the bark of *Styrax Benzo*, a tree growing in Sumatra, Java, Borneo, and Java. From this substance the benzoic acid may be extracted by sublimation in an iron pan (fig. 176) having a sheet of bibulous paper pierced with pinholes stretched over its mouth, and covered with a cap of stout paper. A more productive method is to boil the powdered benzoin with slaked lime and

the filtered and concentrated solution of calcium benzoate with hydrochloric acid. The benzoic acid thus precipitated may be purified by sublimation.

Benzoic acid is inodorous when cold, but acquires a faint smell when gently warmed; it melts at 120°C . (248°F .), and sublimates at a temperature a little above; boils at 250°C . (482°F .). It dissolves in about 20 parts of cold and 25 parts of boiling water, and with great facility in alcohol. Benzoic acid is not affected by ordinary nitric acid, even at boiling heat; but with fuming nitric acid it forms a substitution-product.—Chlorine also acts on benzoic acid, forming substitution-products.—Benzoyl chloride converts it into benzoyl chloride, $\text{C}_6\text{H}_5\text{OCl}$.—Benzoic acid dissolves in ordinary strong sulphuric acid, but is precipitated unaltered on addition of water. By fuming sulphuric acid, however, and still more readily by sulphuric oxide, it is converted into sulphobenzoyl acid.

$C_7H_6SO_3$ (p. 903). By nascent hydrogen (evolved by sodium amalgam) it is partly reduced to benzoic aldehyde and benzylic alcohol, and is partly converted, by addition of hydrogen, into hydrobenzoic acid, $C_7H_{10}O_2$, a crystalline acid which forms a crystalline calcium salt, $Ca(C_7H_9O_2)_2$, and, when recrystallized either in the free state or in the form of calcium salt, is ultimately converted by oxidation into benzoic acid; its ethylic ether, $C_2H_5.C_7H_9O_2$, has the odor of ethyl valerate.

All the benzoates are more or less soluble: they are easily formed, either directly or by double decomposition. The *benzoates of the alkalis* and of ammonia are very soluble, and somewhat difficult to crystallize.—*Calcium benzoate* forms groups of small colorless needles, which require 20 parts of cold water for solution; the *barium salt* dissolves with difficulty in the cold. Neutral *ferric benzoate* is a soluble compound; but the basic salt obtained by neutralizing as nearly as possible with ammonia a solution of ferric oxide, and then adding ammonium benzoate, is quite insoluble. Iron is sometimes thus separated from other metals in quantitative analysis. Neutral and basic *lead benzoate* are freely soluble in the cold. *Silver benzoate* crystallizes in thin transparent plates, which blacken on exposure to light.

Calcium benzoate is resolved by dry distillation into calcium carbonate and benzene, or benzophenone, $C_{12}H_{10}O$, the ketone of benzoic acid $(C_7H_5O_2)_2Ca = CO_2Ca + CO(C_6H_5)_2$. On the other hand, benzoic acid, distilled with excess of lime, is resolved into carbon dioxide and benzene: $C_7H_5O_2 = CO_2 + C_6H_6$.

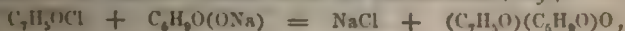
Benzoic Chloride, or Benzoyl Chloride, C_7H_5OCl , is prepared by the action of phosphorus pentachloride on benzoic acid. It is a colorless liquid of disagreeable pungent odor; sp. gr. 1.106; boiling point, $199^\circ C.$ ($390.2^\circ F.$). The vapor is inflammable, and burns with a greenish flame. Benzoyl chloride is decomposed, slowly by cold and quickly by boiling water, into benzoic and hydrochloric acids; with an alkaline hydroxide, a benzoate and chloride of the alkali-metal are produced.

Benzoyl cyanide, $C_6H_5.CO.CN$, obtained by distilling the chloride with potassium cyanide, crystallizes in large plates, melts at $31^\circ C.$ ($87.8^\circ F.$), and boils at $206^\circ-208^\circ C.$ ($402.8^\circ-406.4^\circ F.$). By boiling with alkalis, it is resolved into benzoic and hydrocyanic acids.

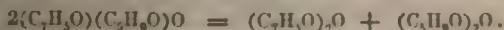
Benzoic Oxide, or Anhydride, $C_{14}H_{10}O_3$ or $(C_7H_5O)_2O$, is obtained by the action of benzoyl chloride on potassium benzoate:



Benzoyl chloride acts in like manner on acetate or valerate of sodium, forming aceto-benzoic or valero-benzoic oxide, either of which splits up on distillation into acetic or valeric oxide and benzoic oxide: *e. g.*,

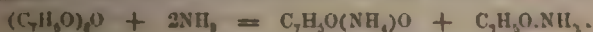


and



Benzo-*onanthylic*, benzo-*stearic*, benzo-*angelic*, benzo-*cuminic* oxide, and several others, have been obtained by similar processes.

Benzoic oxide crystallizes in oblique rhombic prisms, melting at $42^\circ C.$ ($107.6^\circ F.$), and distilling undecomposed at $310^\circ C.$ ($590^\circ F.$). It melts in boiling water, remaining fluid for a long time, but is ultimately converted into benzoic acid, and dissolves: caustic alkalis effect the conversion much more rapidly. With ammonia it forms ammonium benzoate and benzamide:



Benzoyl Dioxide, or Peroxide, $C_6H_5O_2$, or $(C_6H_5O)_2O_2$.—Bestie obtained this compound by bringing benzoyl chloride in contact with barium dioxide under water; the product, when recrystallized from ether, yields large shining crystals of benzoyl dioxide, which explode when heated. Boiled with potash-solution, it gives off oxygen, and forms potassium benzoate.

Thiobenzoic Acid, $C_6H_5.CO.SH$, formed by the action of benzoyl chloride on alcoholic potassium sulphide, is crystalline, melts at $240^\circ C.$ ($464^\circ F.$), and distils with aqueous vapor. Its ethylic ether boils at $245^\circ C.$ ($469.4^\circ F.$).

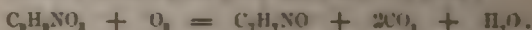
Benzoyl monosulphide, $(C_6H_5O)_2S$, formed by the action of benzoyl chloride on thiobenzoic acid, crystallizes from ether in large prisms, melting at $48^\circ C.$ ($118.4^\circ F.$), and distilling without decomposition. The disulphide, $(C_6H_5O)_2S_2$, produced by oxidation of thiobenzoic acid when its ethereal solution is exposed to the air, forms shining crystals melting at $129^\circ C.$ ($262.4^\circ F.$).

Dithiobenzoic acid, $C_6H_5.CS.SH$, is formed by boiling the compound $C_6H_5.CCl_3$ with an alcoholic solution of potassium sulphide:

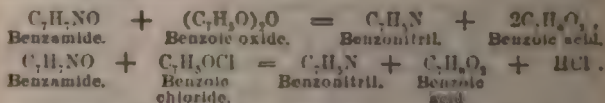


The free acid is very unstable: its lead salt crystallizes from carbon sulphide in red needles.

Benzamide, $C_7H_7NO = C_6H_5.CO.NH_2$, is formed (similarly to acetamide, p. 776) by the action of aqueous ammonia on benzoyl chloride or ethyl benzoate; also by oxidizing hippuric acid with lead oxide:



Benzamide crystallizes in nacreaous laminae, nearly insoluble in cold water, easily soluble in boiling water, also in alcohol and ether. It melts at $125^\circ C.$ ($257^\circ F.$), and volatilizes undecomposed between 280° and $290^\circ C.$ (546.8° and $554^\circ F.$). Its reactions are, for the most part, similar to those of acetamide. Heated with benzoic oxide or chloride, it yields benzonitril and benzoic acid:



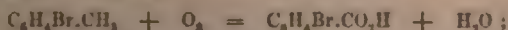
Heated with fuming hydrochloric acid, it forms hydrochloride of benzamide, $C_7H_7NO.HCl$, which separates on cooling in long aggregated prisms. Its aqueous solution dissolves mercuric oxide, forming benzomercuriamide, $C_6H_5.CO.NHg$. By distillation with PCl_3 or P_2S_5 , it is converted into benzonitril.

Phenyl-benzamide, $C_6H_5.CO.NH(C_6H_5)$, is formed by the action of aniline on benzyl chloride.

SUBSTITUTED BENZOIC ACIDS.

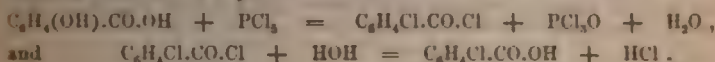
The action of chlorine and bromine on benzoic acid gives rise, for the most part, only to mono-substituted derivatives, $C_6H_4X.CO_2H$, belonging to the meta-series (Cl or Br and CO_2H in the relative positions 1, 3, 5, with nitric acid (diluted with 3 parts of water) meta-derivatives are also produced, together with small quantities of the ortho- and para-

pounds. These and all the other mono-halogen- and mono-nitro-derivatives of benzoic acid may also be formed by oxidation of the corresponding derivatives of toluene; *e. g.*,



the meta- and para-compounds by chromic acid, the ortho-compounds by dilute nitric acid; these last compounds are attacked with difficulty by chromic acid, and then completely broken up.

The halogen-derivatives of benzoic acid may also be formed from the corresponding amidobenzoic acids, by substitution of Cl, etc., for NH_2 , through the medium of the diazo-compounds; and the monochlorine- and monobromine-derivatives by treating the corresponding oxy-acids, $\text{C}_6\text{H}_4(\text{OH}).\text{CO}_2\text{H}$ with PCl_5 or PBr_5 , and decomposing the resulting chloride or bromide with water; *e. g.*,



The ortho-derivatives of benzoic acid fuse at lower temperatures than the corresponding meta- and para-derivatives. They are moderately soluble in water, and form easily soluble barium salts, by means of which they may be separated from the meta- and para-derivatives.

Monochlorobenzoic Acids, $\text{C}_6\text{H}_4\text{ClO}_2$.—The ortho-compound, $\text{C}_6\text{H}_3\text{ClO}_2$, (*Chlorosalicylic acid*), prepared by treating salicylic acid (*o*-oxybenzoic acid) with PCl_5 , and decomposing the resulting chloride with boiling water, crystallizes in colorless needles, melts at 137°C . (278.6°F .), also under boiling water, and is more soluble in water than the meta- and para-compounds.

The meta-compound, $\text{C}_6\text{H}_4\text{ClO}_2$, is formed by oxidation of meta-chlorotoluene; by heating benzoic acid with hydrochloric acid and manganese dioxide or potassium chlorate, or with solution of bleaching powder or with antimonie chloride; also by decomposition of chlorohippuric acid; and from (1 : 4) chloronitrobenzene by means of potassium cyanide. It crystallizes in colorless needles, melting without decomposition at 152°C . (305.6°F .), very slightly soluble in boiling water.

The para-compound, $\text{C}_6\text{H}_4\text{ClO}_2$, (*Chlorodracrylic acid*), formed by oxidation of (1 : 4) chlorotoluene, sublimes in colorless scales, which melt at $236^\circ\text{--}237^\circ \text{C}$. ($456.8^\circ\text{--}458.6^\circ \text{F}$.).

Dichlorobenzoic Acids, $\text{C}_6\text{H}_2\text{Cl}_2\text{CO}_2\text{H}$.—Two modifications (out of six) are known, viz. (a) 1 : 3 : 4 (CO_2H in 1), formed from benzoic acid, and from (1 : 3) or (1 : 4) chlorobenzoic acid by boiling with solution of bleaching powder, or by heating with antimonie chloride; also by oxidation of (1 : 3 : 4) dichlorotoluene with chromic acid. Colorless needles, melting at 202°C . (395.6°F .), slightly soluble in water. (b) (1 : 2 : 3), produced, like the *a*-acid, from (1 : 2) chlorobenzoic acid, and together with the *a*-acid, by treating benzoic acid with HCl and ClO_3K , or with solution of bleaching powder. The two acids may be separated by means of their barium salts, the *b*-salt being the more soluble of the two. The *b*-acid forms slender, shining needles, melts at 150°C . (302°F .), boils at 301°C . (573.8°F .), dissolves in about 1200 parts of water at 110°C . (51.8°F .), more easily in boiling water.

Trichlorobenzoic acid, $\text{C}_6\text{HCl}_3\text{CO}_2\text{H}$, formed by oxidation of trichlorotoluene, crystallizes in small needles melting at 163°C . (325.4°F .), nearly insoluble in cold water. An isomeric acid, formed by heating

dinitro-paramidobenzoic acid with fuming hydrochloric acid, melts at 205° C. (397.4° F.), and sublimes without decomposition.

Mono-bromobenzoic Acid, $C_6H_4Br.CO_2H$ (1 : 2), from ortho-bromotoluene with nitric acid, or from *o*-amidobenzoic acid by heating the diamperbromide with HBr, sublimes in needles, and melts at 147–148° C. (296.6°–298.4° F.). Its barium-salt is very soluble in water. (1 : 1) or ordinary bromobenzoic acid, from metabromotoluene, and by heating benzoic acid with bromine and water to 126°–130° C. (248–266° F.), sublimes in needles, and melts at 155° C. (311° F.). (1 : 4) from parametabromotoluene, is nearly insoluble in water, crystallizes in needles, and melts at 251° C. (483.8° F.).

Di-, tri-, and penta-bromobenzoic acids are formed by heating benzoic acid with bromine to 200° C. (392° F.) and above. $C_6H_2Br_2O_2$ (1 : 3) forms small needles melting at 229°–230° C. (444.2°–446° F.). $C_6H_2Br_3O_2$ and $C_6H_2Br_4O_2$ melt between 234° and 235° C. (453.2°–455° F.).

Mono-iodobenzoic Acids, $C_6H_4I.CO_2H$, are obtained by oxidation of iodotoluenes with nitric acid, or from the corresponding amidobenzoic acids by decomposing the diazo-compounds with hydrotic acid :

(1 : 2) form needles, melting at 157° C. (314.6° F.) ; converted by fusion with potash into salicylic acid.

(1 : 3) sublimes in needles, melting at 187° C. (368.6° F.) ; converted by fusion with potash into oxybenzoic acid.

(1 : 4) sublimes in scales, melts at about 267° C. (512.6° F.), converted by fusion with potash into para-oxybenzoic acid.

Fluobenzoic acid, $C_6H_4F.CO_2H$, produced by treating diazo-amidobenzoic acid with hydrofluoric acid, crystallizes in rhombic prisms melting at 152° C. (359.6° F.).

Mononitrobenzoic Acids, $C_6H_4(NO_2).CO_2H$.—When benzoic acid is treated with fuming nitric acid, or better, with a mixture of nitric (3 parts) and strong sulphuric acid (3 parts) to 1 part of benzoic acid, the chief product obtained is metanitrobenzoic acid, the ortho-compound being formed in smaller, and the para- in very small quantity—the mass being warmed till it melts, and the liquid mass poured off from the solid potassium sulphate. The three nitro-acids are separated by the different solubilities of their barium-salts—that of the ortho-acid being very soluble, that of the meta-acid rather sparingly, and that of the para-acid very slightly soluble. Cinnamic acid yields by nitration two nitroacids, $C_6H_3(NO_2)_2O_2$, *ortho*- and *para*-, from which the corresponding nitrobenzoic acids may be obtained by oxidation. Hippuric acid yields by nitration a nitro-hippuric acid, convertible into metanitrobenzoic acid.

(1 : 2) Nitrobenzoic acid crystallizes in needles or prisms, soluble in 144 parts of water at 16.5° C. (61.7° F.), melting at 145° C. (293° F.). (1 : 3) Nitrobenzoic acid crystallizes in needles or laminae, dissolves in 42 parts of water at 16.5° C. (61.7° F.), sublimes in white needles, melts at 142° C. (287.6° F.). (1 : 4) Nitrobenzoic acid, formed also by oxidation of paranitrotoluene, crystallizes in yellowish laminae, very slightly soluble in water, melting at 24° C. (46.4° F.).

Dinitrobenzoic Acids, $C_6H_3(NO_2)_2.CO_2H$.—Orthonitrobenzoic acid, treated with a mixture of nitric and sulphuric acids, yields three dinitrobenzoic acids (α , β , and γ), easily separated by the unequal solubility of their barium-salts—that of α being very slightly soluble in cold water, that of β moderately, and that of γ very easily soluble. The β -acid is also

produced by oxidation of (1 : 2 : 4) dinitrotoluene (melting point 70.5°C . 158.9°F .) with chromic acid. A fourth acid, δ , is obtained by the action of nitric and sulphuric acid on meta-nitrobenzoic acid.— α (1 : 2 : 3).^{*} Colorless prisms, melting at 177°C . (350.6°F .), moderately soluble in hot, sparingly in cold water. β . (1 : 2 : 4) Long rhombic plates or prisms melting at 179°C . (354.2°F .). γ . (1 : 2 : 6) Slender, white tilted needles, melting at 202°C . (395.6°F .), resolved at a higher temperature into (1 : 3) dinitrobenzene and CO_2 . δ . (1 : 3 : 5) Crystallizes from water in large square plates; from alcohol in prisms.

By reduction with tin and HCl , the α - and δ -compounds yield the corresponding diamidobenzoic acids, whereas β and γ yield no diamido-acids, but (1 : 3) diamidobenzene and CO_2 .

Nitro-chloro- and Nitro-bromobenzoic acids are obtained by nitration of chloro- and bromo-benzoic acids. (1 : 3) bromobenzoic acid yields two (bromometabromobenzoic acids,—one melting at 248°C . (478.4°F .), the other at 141°C . (285.8°F .). In both of them the NO_2 -group is in the ortho-position (2 or 6) with respect to the CO_2H , and both yield by reduction (1 : 2) amidobenzoic acid.

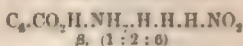
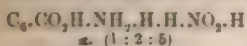
Amidobenzoic Acids, $\text{C}_6\text{H}_4(\text{NH}_2).\text{CO}_2\text{H}$.—The three modifications are formed by reduction of the three nitrobenzoic acids, best by gentle heating with tin and hydrochloric acid. At the end of the reaction the product is diluted with water, precipitated with excess of sodium carbonate, and the concentrated filtrate is acidulated with acetic acid. The ortho-compound is also produced by boiling indigo (1 part) for several days with soda-lye of specific gravity 1.38 (10 parts), gradually adding pulverized manganese dioxide, and renewing the water as it evaporates, till the color of the mass has become light yellow. The product is then dissolved in water, the solution is neutralized with sulphuric acid, filtered, and evaporated to dryness; the residue is exhausted with alcohol; and the salt which remains after evaporation of the alcohol is dissolved in hot water and decomposed with acetic acid.

The three amidobenzoic acids react like glycocine (amidacetic acid), and yield well-characterized salts, both with metallic oxides and with acids. When heated above their melting points they are resolved into aniline and carbon dioxide.

Ortho- (Anthranilic acid).—Thin colorless prisms or laminae, sparingly soluble in cold water, easily in hot water and in alcohol; melts at 144°C . (291.2°F .). *Meta-*. Small colorless needles, united in nodular groups; easily soluble in hot, sparingly in cold water, melts at 173°C – 174°C . (343.4° – 345.2°F .). *Para- (amidodracrylic acid).* Long slender shining needles, easily soluble in water, melting at 186° – 187°C . (366.8° – 368.6°F .).

Nitro-amidobenzoic acids, $\text{C}_6\text{H}_3(\text{NO}_2)\text{C}(\text{NH}_2)\text{CO}_2\text{H}$.

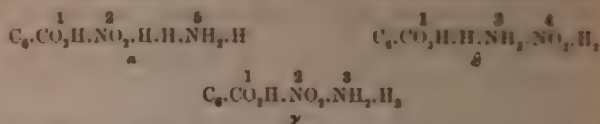
1. Nitro-orthamidobenzoic acid is known in two modifications, viz.:



which are produced from the corresponding nitrosalicylic acids by heating their diethylic ethers with alcoholic ammonia, and decomposing the resulting nitramidobenzamides, $\text{C}_6\text{H}_3(\text{NO}_2)(\text{NH})_2\text{CO.NH}_2$, with boiling baryta-water. Both acids crystallize in long needles, the α -acid melting at 170°C . (516°F .), the β -acid at 205°C . (401°F .).

* CO_2H in 1.

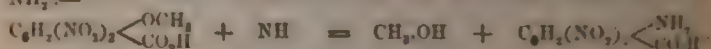
2. *Nitro-metamidobenzoic acid* is known in three modifications, viz. —



They are obtained by boiling the three dinitro-uramidobenzoic acids (p. 902) with water. All three crystallize in yellow needles, α and β sparingly soluble in hot water, γ easily soluble.

3. *Nitro-paramidobenzoic acid* (1 : 3 : 4), obtained in like manner from dinitro-para-uramidobenzoic acid, or by heating nitranisic acid with aqueous ammonia to 140°–170° C. (284°–335° F.) for three or four hours, forms small deep-yellow needles, slightly soluble in boiling water, melting at 284° C. (543.2° F.).

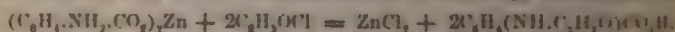
Dinitro-paramidobenzoic acid, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH}_2$, or *Chrysanic acid*, is produced by heating dinitro-anisic or dinitro-ethylparaoxybenzoic acid with aqueous ammonia, the group OCH_3 or OC_2H_5 being thus replaced by NH_2 :—



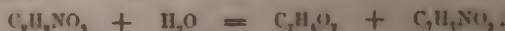
It crystallizes in shining golden-yellow needles, melts at 259° C. (498.2° F.) and sublimes; is nearly insoluble in cold water, moderately soluble in boiling water and in alcohol. It is a strong monobasic acid.

Dinitro-orthoamidobenzoic acid, obtained in like manner from dinitroethylsalicylic acid, crystallizes from alcohol, in which it is slightly soluble, as golden-yellow scales, melting at 256° C. (492.8° F.).

Acetyl-metamidobenzoic acid, $\text{C}_6\text{H}_4\text{NO}_2 = \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{H}_3\text{O}_2$, is formed by digesting (1 : 3) amidobenzoic acid with glacial acetic acid at 160° C. (320° F.), or zinc metamidobenzoate with acetyl chloride at 108°

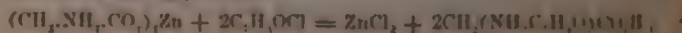


It forms white microscopic crystals, insoluble in cold water and in ether, slightly soluble in boiling water, easily in boiling alcohol, melts at 220–230° C. (438.8°–446° F.), sublimes at 200° C. (392° F.). It is a monobasic acid, forming easily soluble salts with the metals of the alkalis and alkaline earths; sparingly soluble salts with lead, silver, and copper. By boiling with dilute sulphuric acid, it is resolved into acetic and amidobenzoic acids :



Acetyl-paramidobenzoic acid, isomeric with the last, is easily obtained by oxidizing acetoparatoluidine, $\text{C}_6\text{H}_4(\text{NH}_2\text{C}_2\text{H}_5\text{O})\text{CH}_3$, with potassium permanganate. It crystallizes in needles, sparingly soluble in water, more readily in alcohol, and melting with decomposition at about 250° C. (482° F.).

Hippuric or Benzanidacetic acid, $\text{C}_8\text{H}_7\text{NO}_3 = \text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{C}_2\text{H}_3\text{O}_2$ (*Benzoyl glycocine*).—This acid, metameric with the one just described, is formed by the action of benzoyl chloride on the zinc salt of amidacetic acid (glycocine).



the reaction being analogous to the second of those above given for the formation of acetamidobenzoic acid.

Hippuric acid occurs, often in large quantities, in the urine of horses, cows, and other herbivorous animals; in smaller quantity also in human urine. It may be prepared by boiling fresh cows' or horses' urine with milk of lime, and precipitating the concentrated filtrate with hydrochloric acid. For purification the crude acid is washed with chlorine-water; or its solution in dilute soda-lye is boiled with sodium hypochlorite till it becomes colorless, and the solution, after cooling, is precipitated with hydrochloric acid.

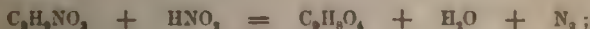
Hippuric acid crystallizes in rhombic prisms, which have a slightly bitter taste and acid reaction, melt on the application of heat, and require for solution about 600 parts of cold water; it also dissolves in hot alcohol. At a high temperature it decomposes, yielding benzoic acid, ammonium benzoate, and benzonitril, with a coaly residue. Boiling hydrochloric acid converts it into benzoic acid and glycocine (amidacetic acid):



just as acetamidobenzoic acid is resolved into acetic and amidobenzoic acids.

Hippuric acid is monobasic, the formula of the hippurates of monatomic metals being $\text{C}_9\text{H}_7\text{MNO}_2$. Most metallic oxides dissolve readily in hippuric acid. The hippurates of potassium, sodium, and ammonium are very soluble, and difficult to crystallize; their solutions form a cream-colored precipitate with ferric salts, and white curdy precipitates with silver nitrate and mercurous nitrate. A characteristic reaction of the hippurates is, that they give off ammonia when fused with excess of potash or lime, and yield benzene by distillation. Mineral acids decompose them, separating the hippuric acid.

Hippuric acid, treated with nitrous acid, gives off nitrogen, and is converted into benzoglycollic acid, $\text{C}_7\text{H}_5\text{O}_4$, an acid containing the elements of benzoic and glycollic (oxyacetic) acids, minus one molecule of water:—



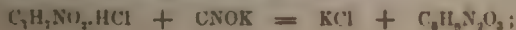
and benzoglycollic acid, when boiled with water, splits up into benzoic and glycollic acids:



If, in the preparation of hippuric acid, the urine be in the slightest degree putrid, the hippuric acid is all destroyed during the evaporation, ammonia is disengaged in large quantity, and the liquid is then found to yield nothing but benzoic acid, not a trace of which can be discovered in the unaltered secretion. When benzoic acid is taken internally, it is rejected from the system in the state of hippuric acid, which is then found in the urine.

Hippuric acid dissolves so abundantly in an aqueous solution of sodium phosphate, that this solution loses its alkaline reaction and becomes acid. This reaction may explain the acid character of the recent urine of man and herbivorous animals.

Uramidobenzoic acid, $\text{C}_8\text{H}_7\text{N}_2\text{O}_2 = \text{CO} \begin{smallmatrix} \text{NH}.\text{C}_6\text{H}_4.\text{CO.OH} \\ \text{NH}_2 \end{smallmatrix}$, is formed by mixing the cold solutions of equivalent quantities of hydrochloride of metamidobenzoic acid and potassium cyanate:



also by fusing urea with metamidobenzoic acid: $C_6H_7NO_2 + CH_4N_2O = NH_4 + C_6H_5N_2O_2$. It crystallizes in small needles, containing 1 molecule of water, soluble in hot water and in alcohol. When heated to $200^\circ C.$ ($392^\circ F.$) it is resolved into H_2O and oxybenzoyl-urea, $C_6H_5N_2O_2 =$

$NH.C_6H_4.CO$
 $CO < \begin{array}{c} NH \\ | \end{array}$. By boiling with caustic potash, it is resolved into amidobenzoic acid, carbon dioxide, and ammonia.

Uramidobenzoic acid, treated with a mixture of nitric and sulphuric acid, yields three isomeric dinitro-uramidobenzoic acids, which, when boiled with water, are converted into three nitro-amidobenzoic acids, α , β , γ (p. 900).

Para-uramidobenzoic acid, formed as above from paramidobenzoic acid, crystallizes in white shining elongated laminæ, but slightly soluble in water even at the boiling heat. By nitration it yields only one dinitro-paramidobenzoic acid, convertible into one nitro-paramidobenzoic acid.

Diamidobenzoic acid, $C_6H_4(NH_2)_2.CO_2H$.—The six possible modifications of this acid have all been obtained, viz. (CO_2H in 1):

1:2:3, 1:2:4, 1:2:5, 1:2:6, 1:3:4, 1:3:5.

The acids 1:2:3 and 1:3:4 are formed from β and γ nitro-metamidobenzoic acid (p. 900), and yield by distillation ortho-diamidobenzene.

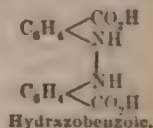
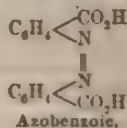
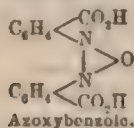
The acids 1:2:6, 1:2:4, and 1:3:5 are formed by reduction of the three dinitrobenzoic acids (pp. 898, 899), and are converted, by elimination of CO_2 , into metadiamidobenzene.

The acid 1:2:5 (or 1:3:6) is formed from α -nitro-metamidobenzoic acid and from the corresponding dinitrobenzoic acid, and is convertible into paradiamidobenzene.

Hence it appears that (1:4) diamidobenzene is producible from only one diamidobenzoic acid: (1:3) diamidobenzene from three; and (1:2) diamidobenzene from two diamidobenzoic acids. This result affords a further confirmation of the structure of the three diamidobenzenes (pp. 813, 857).

A triamidobenzoic acid, $C_6.CO_2H.NH_2.H.NH_2.NH_2.H$, is formed by reduction of (1:2:4:5) dinitramidobenzoic acid. It crystallizes in shining needles containing $\frac{1}{2}H_2O$, and is resolved by distillation into CO_2 and triamidobenzene.

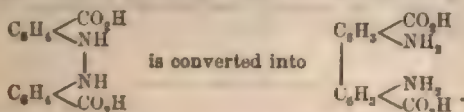
Azobenzoic Acids.—The action of sodium-amalgam on the mononitrobenzoic acids (or rather on their sodium-salts) gives rise (as in the case of nitrobenzene, p. 851) to azo-, azoxy-, and hydrazobenzoic acids:



Metazobenzoic acid, $C_{14}H_{10}N_2O_4 + \frac{1}{2}H_2O$ (CO_2H and N in the relative positions 1, 3), is precipitated by hydrochloric acid from the solution of its sodium salt, as a yellow amorphous powder, very slightly soluble in water, alcohol, and ether; decomposed by distillation. It is bibasic, and forms crystalline yellow salts and ethers. Parazobenzoic acid is a flesh-colored amorphous powder.

Azoxylbenzoic acid, $C_{14}H_{10}N_2O_5$ (1:3), is formed by boiling an alcoholic solution of metanitrobenzoic acid with solid potash, and is precipitated by hydrochloric acid in yellowish crystalline flocks.—Bibasic.

Hydrazobenzoic acid, $C_{14}H_{13}N_2O_4$, is formed by adding ferrous sulphate to a boiling solution of azobenzoic acid in caustic soda-lye, and is precipitated by hydrochloric acid in yellowish flocks, very slightly soluble in hot alcohol. Its salts in aqueous solution absorb oxygen from the air, whereby they are converted into azobenzoates. By boiling with hydrochloric acid it is converted into an isomeric acid derivable from diphenyl, just as hydrazobenzene is converted into benzidine (p. 852):



The last-mentioned acid is resolved by distillation into CO_2 and benzidine.

Diazo-derivatives of Benzoic Acid.—These compounds are formed from the amidobenzoic acids in the same manner as the diazobenzene-compounds from the amidobenzenes.

Diazobenzoic Nitrate, $C_6H_5 < \begin{array}{c} N=N.NO_2 \\ CO_2H \end{array}$, is formed by the action of nitrous acid on a solution of metamidobenzoic acid in nitric acid. It is sparingly soluble in cold water, and separates therefrom in colorless prisms, which explode violently when heated. Potash added to the aqueous solution throws down a yellow, very unstable mass, probably consisting of free diazobenzoic acid $[C_6H_5 < \begin{array}{c} CO_2H \\ N=N.OH \end{array}]$. The nitrate boiled with water yields meta-oxybenzoic acid. Bromine-water added to the aqueous solution throws down the perbromide, $C_6H_5N_2O_4Br_3$, as an oil which solidifies in yellow prisms, and is resolved by heating with alcohol into nitrogen, bromine, and metabromobenzoic acid.

Diazo-amidobenzoic acid, $C_{14}H_{11}N_3O_4 = C_6H_5 < \begin{array}{c} N=N-NH-C_6H_5-CO_2H \\ CO_2H \end{array}$, is precipitated, on passing nitrous acid into the alcoholic solution of metamidobenzoic acid, as an orange-red crystalline powder, nearly insoluble in water, alcohol, and ether. It is a weak basic acid, and its salts in aqueous solution are very unstable. The acid, heated with haloid acids, yields the corresponding halogen-derivatives of benzoic acid.

Diazo- and diazo-amido-compounds of exactly similar character are obtained from ortho- and para-amidobenzoic acid.

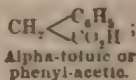
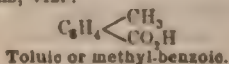
Sulphobenzoic Acids, $C_6H_5 < \begin{array}{c} CO_2H \\ SO_3H \end{array}$. — When vapor of sulphuric anhydride is passed over dry benzoic acid, and the product is treated with water, or when benzoic acid is heated for a considerable time with fuming sulphuric acid, the chief product formed is *meta*-sulphobenzoic acid, the *para*-acid being also produced in small quantity. The latter is obtained in the pure state by oxidation of *para*-toluenesulphonic acid (p. 860), or *para*-sulphocinnamic acid, with chromic acid mixture.

The *meta*-acid is a colorless, crystalline, very deliquescent, strongly acid mass, converted by distillation with PCl_5 into meta-chlorobenzoyl chloride. It is a very stable dibasic acid: its neutral barium salt is very soluble. The *para*-acid, $C_6H_5SO_3$, crystallizes in non-deliquescent needles, melting above $200^\circ C.$ ($392^\circ F.$), and decomposing even at a lower temperature. Its neutral barium salt, $C_6H_5SO_3Ba + 2H_2O$, crystallizes in small, ramified, easily soluble needles.

Chloro- and Bromo-sulphobenzoic acids are obtained by the action of fuming sulphuric acid on the corresponding derivatives of benzoic acid, and by oxidation of chloro- and bromo-toluene-sulphonic acids.

Disulphobenzoic acid, $C_6H_4(CO_2H)(SO_3H)_2$, is formed by heating benzoic acid with fuming sulphuric acid and phosphoric anhydride to 250° C. (482° F.). Deliquescent acicular prisms. Tribasic. By distillation with potassium cyanide, it yields a dicyanide, m. p. 159° C. (318.2° F.), convertible into isophthalic acid. An isomeric disulpho-acid is formed by oxidation of toluenedisulphonic acid.

Toluic Acids, $C_8H_8O_2$.—Of these acids there are two metameric modifications, viz.:



the first admitting of the three isomeric modifications, *o*-, *m*-, *p*-. These three toluic acids are formed by oxidation of the corresponding dimethyl-benzenes (xylenes) with nitric acid diluted with 3 volumes of water; also from the corresponding cyanotoluenes, $C_6H_4(CN).CH_3$, by the action of alcoholic potash, or of strong hydrochloric acid. By oxidation with chromic acid mixture, or potassium permanganate, they are converted into the corresponding phthalic acids, $C_8H_6(CO_2H)_2$.

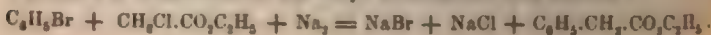
Orthotoluic acid crystallizes in long slender needles melting at 102.5° C. (215.6° F.); is moderately soluble in hot water, and distils easily with aqueous vapor. By oxidation with permanganate it yields phthalic acid, whereas chromic acid mixture oxidizes it completely to carbonic acid. Its calcium salt, $(C_8H_7O_2)_2Ca + 2H_2O$, and barium salt, $(C_8H_7O_2)_2Ba$, form slender needles easily soluble in water.

Metatoluic acid is best obtained from cyanotoluene, or by the action of sodium-amalgam on bromometatoluic acid. It is more soluble in water than its two isomerides, and crystallizes from hot water in slender needles, melting at 109°–110° C. (228.2°–230° F.); distils easily with aqueous vapor. Chromic acid mixture oxidizes it readily to isophthalic acid. Its calcium salt, $(C_8H_7O_2)_2Ca + 3H_2O$, crystallizes from alcohol in needles, easily soluble in water.

Bromometatoluic acid, $C_8H_7BrO_2$, is formed by heating nitropara-bromotoluene with alcoholic potassium cyanide to 220° C. (428° F.), and separating the product with potash.

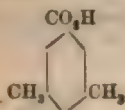
Paratoluic acid, obtained by oxidation of (1 : 4) xylene, or of cymene, with dilute nitric acid, crystallizes in needles melting at 178° C. (352.4° F.). Its calcium salt, $(C_8H_7O_2)_2Ca + 2H_2O$, forms needles easily soluble in water. Chromic acid mixture oxidizes it to terephthalic acid.

Alpha-toluic or Phenyl-acetic acid, $C_6H_5.CH_2.CO_2H$, is formed by boiling benzyl cyanide, $C_6H_5.CH_2.CN$, with alkalis; by heating mandelic acid, $C_6H_5.CH(OH).CO_2H$, with hydriodic acid; by boiling vulpic acid, $C_9H_9O_3$ (p. 918), with baryta; and as an ethylic ether, by heating a mixture of bromobenzene and ethyl chloroacetate with sodium:

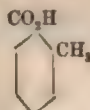


It crystallizes from boiling water in broad thin laminae, very much like benzoic acid; smells like horse-sweat; melts at 76.5°C . (167.90°F .), and boils at 261°C .– 262°C . (501.8°C .– 503.6°F .). By distillation with PCl_5 it yields the chloride $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{COCl}$, which passes over as a colorless heavy liquid. By oxidation with chromic acid mixture it yields benzoic acid.

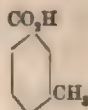
Acids, $\text{C}_9\text{H}_{10}\text{O}_2$.—Of the six possible dimethyl-carbonic acids, $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{CO}_2\text{H}$, three are known, viz.:



Mesitylenic.



Xylic.



Paraxylic.

Mesitylenic acid (1 : 3 : 5), formed by oxidizing mesitylene with dilute nitric acid, crystallizes from alcohol in large prisms, from water in needles; melts at 166°C . (330.8°F .), and sublimes without decomposition. Distilled with excess of lime it yields isoxylene. By nitric acid it is further oxidized to trimesic and uvitic acids. Its *barium-salt*, $(\text{C}_6\text{H}_3\text{O}_2)_2\text{Ba}$, dissolves easily in water, and forms large shining prisms. The *ethyl ether*, $\text{C}_9\text{H}_9\text{O}_2\cdot\text{C}_2\text{H}_5$, solidifies at 0° , and boils at 241°C . (465.8°F .).

Xylic acid (1 : 2 : 4), and paraxylic acid (1 : 3 : 4), are formed, together with bibasic xylic acid, $\text{C}_6\text{H}_2(\text{CH}_3)_2(\text{CO}_2\text{H})_2$, by oxidizing pseudocumene (p. 819) with dilute nitric acid at the boiling heat. At the end of the reaction a crystalline mass separates, and on repeatedly boiling this mass with water, xylic and paraxylic acids pass over, while xylic acid and nitro-acids remain behind. The xylic and paraxylic acids are separated by the different solubility of their calcium salts, the xylate being the more soluble of the two. Both acids crystallize in prisms, xylic acid melting at 126°C . (258.8°F .), paraxylic acid at 163°C . (325.4°F .). Xylic acid is more soluble in water than paraxylic acid. Both acids dissolve easily in alcohol.

Alphaxylic acid, $\text{C}_6\text{H}_4(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H}$, is obtained by boiling xylyl chloride with potassium cyanide (whereby xylyl cyanide, $\text{C}_6\text{H}_4\text{CN}$, is produced), and then with potash. It crystallizes in broad needles, having a satiny lustre, easily soluble in water, and boiling at 420°C . (107.6°F .).

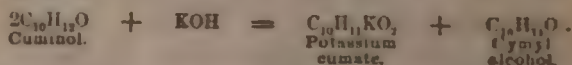
Ethyl-benzoic acid, $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)_2\text{CO}_2\text{H}$ (1 : 4), obtained by oxidation of para-diethylbenzene with nitric acid, and from bromethylbenzene by the action of Na and CO_2 , crystallizes from hot water in slender laminae melting at 110°C . (230°F .), and easily subliming. By oxidation it yields terephthalic acid.

Hydrocinnamic, Phenylpropionic, or Homotoluic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, is formed by the action of sodium-amalgam, or of very strong hydriodic acid at 100° , on cinnamic acid, $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{H}$, also by heating chloroethyl-benzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Cl}$ (p. 827), with potassium cyanide, and boiling the resulting nitril with potash. It crystallizes in slender needles, easily soluble in hot water and in alcohol, melts at 47°C . (116.6°F .), and distils without decomposition at 280°C . (536°F .). By oxidation it yields benzoic acid. Heated to 160°C . (320°F .) with bromine, it is reconverted into cinnamic acid: $\text{C}_6\text{H}_5\text{O}_2 + \text{Br}_2 = 2\text{HBr} + \text{C}_6\text{H}_5\text{O}_2$.

Hydro-atropic acid, $C_6H_5.CH \begin{smallmatrix} CH_3 \\ \diagup \\ CO_2H \end{smallmatrix}$, formed by the action of sodium amalgam on atropic acid, is a thick oily liquid.

Acids, $C_{10}H_{12}O_2$.—*Durylic acid*, $C_6H_5(CH_2)_3.CO_2H$, formed by oxidizing durenene, $C_6H_5(CH_2)_4$, with dilute nitric acid, crystallizes in hard prisms melting at $150^\circ C.$ ($302^\circ F.$), and is converted by oxidation into cumidic acid.

Cumic acid, $C_6H_5(C_2H_5).CO_2H$ (1:4), is obtained by oxidation of cuminol or cumic aldehyde, $C_{10}H_{12}O$, or by heating this aldehyde with alcoholic potash:



It crystallizes in needles and laminæ, dissolves easily in hot water and in alcohol, melts at $113^\circ C.$ ($235.4^\circ F.$), boils at about $230^\circ C.$ ($454^\circ F.$). By distillation with lime it yields cumene, C_9H_{10} , and by oxidation with chromic acid it is converted into terephthalic acid.

Alphacymic acid, $C_{11}H_{14}O_2$, probably $C_6H_5(CH_2)_3.CH_2.CO_2H$, is formed by the action of caustic alkalies on cymyl cyanide, $C_{14}H_{18}.CN$.

MONATOMIC ACIDS, $C_nH_{2n-10}O_2$

The acids of this series are unsaturated compounds, related to benzoic acid and its homologues, in the same manner as those of the acrylic series to the fatty acids.

Cinnamic Acid, $C_9H_8O_2 = C_6H_5.CH=CH.CO_2H$ (*Phenyl-acrylic acid*).—This acid is produced synthetically: 1. By heating benzoic aldehyde in close vessels with acetyl chloride:

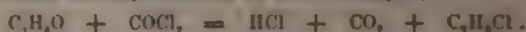


2. By heating the same aldehyde with acetic anhydride and sodium acetate:



The mode of action in this case is not well understood, but the presence of the sodium acetate appears to be essential.

3. By treating potassium benzoate with chloroethylene, C_2H_2Cl (produced by the action of carbonyl chloride on acetic aldehyde):



and



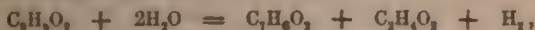
4. By the action of sodium and carbon dioxide on monobromo-cinnamene:



5. Cinnamic acid is also produced by oxidation of cinnamene-oil (cinnamic aldehyde, C_9H_8O) in air or oxygen, and exists ready formed, together with benzoic acid, and certain oily and resinous substances, in Peru and Tolu balsams—the produce of certain South American *Myroxylon*—

being doubtless formed by oxidation of cinnyl alcohol or styrene, $C_9H_{10}O$ (p. 886), likewise contained therein. It is easily prepared by mixing pulverized Tolu balsam with an equal weight of slaked lime, filtering hot, and decomposing the calcium cinnamate, which crystallizes out on cooling, with hydrochloric acid. The mother-liquid contains calcium benzoate.

Cinnamic acid crystallizes from hot water in slender needles, from alcohol in thick prisms. It is inodorous, melts at $133^\circ C.$ ($271.4^\circ F.$), and distills almost without decomposition at $230^\circ C.$ ($554^\circ F.$). It is much less soluble in water than benzoic acid, but dissolves easily in alcohol. It is oxidized by nitric acid to benzoic acid and benzoic aldehyde; by chromic acid chiefly to benzoic acid. By fusion with excess of potash it is resolved into benzoic and acetic acids:



the decomposition being precisely analogous to that of an acid of the acrylic series into two acids of the fatty series (p. 715). By distillation with lime or baryta, and partly also when distilled alone, it is resolved into carbon dioxide and cinnamene, C_9H_8 (p. 821).

The metallic cinnamates, $C_9H_7MO_2$ (for monatomic metals), are very much like the benzoates.

Ethyl Cinnamate, $C_9H_7O_2.C_2H_5$, obtained by passing gaseous hydrogen chloride into a solution of cinnamic acid in absolute alcohol, is a liquid boiling at $267^\circ C.$ (512.6°).

Benzyl Cinnamate or *Cinnamein*, $C_9H_7O_2.C_7H_7$, is contained in Pern and Tolu balsams, in small quantity also in storax, and may be formed artificially by heating sodium cinnamate with benzyl chloride. It crystallizes in shining prisms melting at $39^\circ C.$ ($102.2^\circ F.$), distilling without decomposition only under reduced pressure.

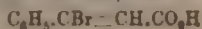
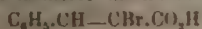
Cinnyl Cinnamate or *Styracin*, $C_9H_7O_2.C_9H_9$, occurs, together with cinnamene, in liquid storax (which exudes from *Styrax calamita*, a shrub growing in Greece and Asia Minor), and may be obtained therefrom by distilling the balsam to expel the cinnamene, then boiling it with aqueous sodium carbonate to remove free cinnamic acid, and kneading the spongy residue between the fingers. The styracin then runs out as an oily liquid, and may be obtained in tufts of prisms by crystallization from alcohol. By distillation with potash it is resolved into cinnyl or styryl alcohol, $C_9H_{10}O$, and cinnamic acid.

Addition-products of Cinnamic Acid.—This acid, like other unsaturated compounds, can take up H_2 , HBr , $ClOH$, etc.; thus it is converted by sodium-amalgam into hydrocinnamic acid, $C_9H_{10}O_2$ (p. 905).

Cinnamic Dibromide, $C_9H_8Br_2O_2 = C_6H_5.CHBr.CHBr.CO_2H$, formed by the action of bromine vapor on cinnamic or on hydrocinnamic acid, crystallizes from alcohol in rhombic laminae, melting, with decomposition, at about $195^\circ C.$ ($383^\circ F.$). By boiling with water it is resolved into monobromocinnamene and phenylbromolactic acid, $C_6H_5.CHBr.CH(OH).CO_2H$.

This last mentioned acid is also formed by direct addition of $BrHO$ to cinnamic acid, and phenyl-chlorolactic acid in like manner by addition of $ClOH$. Both these acids are converted, by heating with alcoholic potash, into phenyloxyacrylic or oxycinnamic acid, $C_6H_5.CH=C(OH).CO_2H$, which separates from its salts as an oil, solidifying in shining laminae, and decomposed by heat.

Substitution-products.—Cinnamic dibromide heated with alcoholic potash yields two isomeric monobromocinnamic acids, viz.:



Both are crystalline. The α -acid melts at 130° C. (266° F.), and forms salts which crystallize readily; the β -acid melts at 120° C. (248° F.) and forms deliquescent salts. α unites with 2 atoms of bromine, and is converted by sodium-amalgam into hydrocinnamic acid; β is converted into α by distillation, or by heating with hydriodic acid.

Two nitrocinnamic acids (*ortho*- and *para*-) are formed by direct nitration, and may be separated by the different solubilities of their ethyl ethers in cold alcohol, the *p*-compound being nearly insoluble. The *o*-compound melts at 232° C. (449.6° F.), the *p*-compound at 265° C. (509° F.). Both are converted by chromic acid into the corresponding nitrobenzoic acids.

The following homologues of cinnamic acid (which cannot here be described) are formed by heating benzoic and cumic aldehydes with the sodium salt of a fatty acid, $C_nH_{2n}O_2$, and the corresponding anhydride, $(C_nH_{2n-1}O)_2O$, *e. g.*, phenylcrotonic acid from benzoic aldehyde, sodium propionate, and propionic anhydride—the mode of formation being exactly analogous to that of cinnamic acid from C_7H_6O and $C_3H_6O_2$ (p. 906).

| Acids from Benzoic Aldehyde. | | Acids from Cumic Aldehyde. | |
|------------------------------|-------------------|----------------------------|-------------------|
| Phenylcrotonic | $C_{10}H_{10}O_2$ | Cumenylacrylic | $C_{11}H_{10}O_2$ |
| Isophenylcrotonic | $C_{10}H_{10}O_2$ | Cumenyl-crotonic | $C_{11}H_{10}O_2$ |
| Phenyl-angelic | $C_{11}H_{12}O_2$ | Cumenyl-angelic | $C_{12}H_{12}O_2$ |

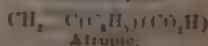
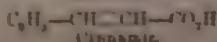
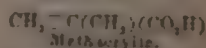
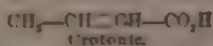
An Isophenylcrotonic acid is formed by the action of succinic anhydride and sodium succinate on benzoic aldehyde:



Sodium-amalgam converts these acids into acids of the series $C_nH_{2n-4}O_2$, *e. g.*, hydrocumenylacrylic, $C_{11}H_{10}O_2$.

Atropic and Isotropic Acids, isomeric with cinnamic acid, are formed simultaneously from tropic acid (p. 930), by boiling with baryta-water or hydrochloric acid: $C_9H_{10}O_2 - H_2O = C_9H_8O_2$.

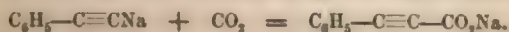
Atropic acid, the chief product formed when baryta is used, crystallizes from hot water in monoclinic plates, slightly soluble in cold water, melting at 106.5° C. (223.7° F.). It is oxidized by chromic acid mixture to benzoic acid, converted by sodium-amalgam into hydroatropic acid (p. 906); and resolved by fusion with potash into alphetonic acid, $C_8H_7CH_2.CO_2H$, and formic acid, whereas cinnamic acid similarly treated yields benzoic and acetic acids; hence it appears that atropic acid is related to cinnamic acid in the same manner as methacrylic to solid crotonic acid (p. 716):



Isotropic acid, probably a polymeric modification, is the chief product obtained by heating tropic acid with hydrochloric acid to 140°C . (284°F .). It forms thin laminæ, very slightly soluble in water, melts at 200°C . (392°F .); does not unite with nascent hydrogen.

Acids, $\text{C}_8\text{H}_{2n-11}\text{O}_3$:—

Phenyl-propionic acid, $\text{C}_8\text{H}_6\text{O}_3 = \text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$, is formed :
 1. By boiling α -bromocinnamic acid with alcoholic potash. 2. By the action of Na and CO_2 on α -bromocinnamene, $\text{C}_6\text{H}_5-\text{C}_6\text{H}_4\text{CH}=\text{CHBr}$. 3. By the action of CO_2 on sodium-acetylenylbenzene (p. 822) dissolved in ether :

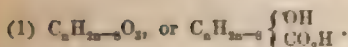


It crystallizes from hot water in long shining needles; melts and sublimes at 136° – 137°C . (276.8° – 278.6°F .); melts under water at 80°C . (176°F .). It is oxidized by chromic acid mixture to benzoic acid; converted by sodium-amalgam into hydrocinnamic acid; resolved by heating with water to 120°C . (248°F .) into CO_2 and phenyl-acetylene, $\text{C}_6\text{H}_5.\text{C}\equiv\text{CH}$ (p. 822).

Homologous with phenyl-propionic acid are the following acids formed from cinnamic aldehyde, $\text{C}_9\text{H}_8\text{O}$, by the action of the anhydrides and sodium salts of fatty acids, viz. :—

| | | | | | |
|--------------------------|---|---|---|---|--|
| Cinnamenyl-acrylic acid | . | . | . | . | $\text{C}_{11}\text{H}_{10}\text{O}_3$ |
| Cinnamenyl-crotonic acid | . | . | . | . | $\text{C}_{17}\text{H}_{12}\text{O}_3$ |
| Cinnamenyl-angelic acid | . | . | . | . | $\text{C}_{13}\text{H}_{14}\text{O}_3$. |

MONOBASIC AND DIATOMIC ACIDS.



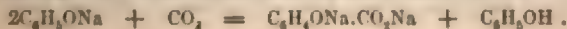
These aromatic oxy-acids, like the corresponding acids of the fatty series (the lactic acids), exhibit alcoholic as well as acid characters. In contact with carbonates they give up only the hydrogen-atom of the CO_2H group in exchange for a metal (forming neutral salts), but when acted upon by strong free bases (caustic alkalis), they likewise exchange the hydrogen of the hydroxyl-group (the alcoholic or phenolic hydrogen) for metals, forming so-called basic salts, e. g., $\text{C}_6\text{H}_4(\text{ONa})(\text{CO}_2\text{Na})$. These, like the metallic derivatives of the phenols, are decomposed by carbonic acid, and converted into neutral salts.

The aromatic oxy-acids are formed from the halogen-derivatives of benzoic acid and its homologues, and from the sulpho-acids, by fusion with alkalis; from the amido-derivatives of the same acids by the action of nitrous acid; and from the phenols by the action of sodium and carbon dioxide.

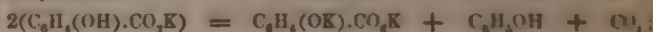
Oxybenzoic Acids, $\text{C}_7\text{H}_6\text{O}_3 = \text{C}_6\text{H}_4(\text{OH}).\text{CO}_2\text{H}$.

1. ORTHO-OXYBENZOIC or SALICYLIC ACID (1 : 2) is formed :

(1) By heating sodium phenate in a stream of carbon dioxide, phenol then distilling over, while disodium salicylate remains behind :



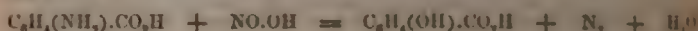
The reaction takes place even below 100° , but proceeds most quickly between 170° and 180° C. (338° and 356° F.), and goes on in the same way up to 300° C. (572° F.), at which temperature the sodium salicylate begins to decompose. This process is applied to the preparation of salicylic acid on the large scale. Potassium phenate heated in a stream of carbon dioxide is decomposed in the same manner, yielding pure dipotassium salicylate up to 150° C. (302° F.); but above that temperature the isomeric paraoxybenzoate is likewise produced, increasing in proportion as the temperature rises, and becoming the sole product at 220° C. (428° F.). Monopotassium salicylate is decomposed in the same manner at 230° (428° F.), yielding a distillate of phenol and a residue of dipotassium paraoxybenzoate:



and the monosodium salt undergoes a similar decomposition, yielding, however, not paraoxybenzoate, but salicylate of sodium.

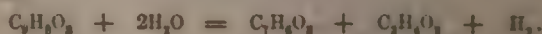
(2) By oxidation of salicylic aldehyde or of saligenin (p. 884).

(3) By the action of nitrous acid on (1 : 2) amidobenzene (anthranilic) acid:



(4) By fusing (1 : 2) chloro- or bromobenzoic acid, or (1 : 2) toluene-sulphonic acid with alkalis.

(5) Together with acetic acid, by heating coumaric acid with potassium hydroxide:



Salicylic acid occurs in the free state in the flowers of meadow-sweet (*Spiraea ulmaria*), and as a methylic ether in oil of winter green (*Gaultheria procumbens*), from which it may be obtained by distillation with potash.

Salicylic acid crystallizes from its alcoholic solution by spontaneous evaporation in large monoclinic prisms. It requires about 1500 parts of cold water to dissolve it, but is much more soluble in hot water and in alcohol. Its aqueous solution imparts a deep violet color to ferric salts. It melts at 155° – 156° C. (311° – 312.8° F.), gives off phenol at a higher temperature, and when heated with pounded glass or quick lime, is completely resolved into carbon dioxide and phenol. It is distinguished from both its isomerides by its behavior with ferric salts, its very slight solubility in water, and its lower melting point. It is a very powerful antiseptic.

Basic Barium salicylate, $\text{C}_6\text{H}_4\langle\text{CO}_2\rangle\text{Ba} + 2\text{H}_2\text{O}$, separates in sparingly soluble laminae on boiling salicylic acid with baryta-water, both the hydroxylic hydrogen-atoms being replaced by barium. The *basic calcium salt* is formed in a similar manner, and separates as an insoluble powder. The reaction affords another distinction between salicylic acid and its isomerides.

Halogen-derivatives of Salicylic acid are easily formed by the direct action of bromine and chlorine; also of iodine, in presence of HgO or Ia_3H . By nitration salicylic acid yields three nitro-acids.

Salicylic chloride, $\text{C}_6\text{H}_4\text{ClCO}_2\text{Cl}$, formed by the action of PCl_5 on the acid, is an oil which boils at 240° C. (464° F.), and is converted by hot water into *o*-chlorobenzoic acid.

Salicylic anhydride or Salicylide, $\text{C}_6\text{H}_4\langle\text{CO}\rangle$, formed by the action of PCl_5 on salicylic acid, crystallizes in shining needles, dis-

lives sparingly in water, and is reconverted by alkalis into salicylic acid.

Salicylamide, $C_6H_4(OH).CO.NH_2$, formed by heating ammonium salicylate, or by the action of ammonia on salicylic ethers forms sparingly soluble laminae melting at $132^\circ C.$ ($269.6^\circ F.$).

Salicylic ethers are formed by passing gaseous hydrogen chloride to the solutions of salicylic acid in the corresponding alcohols. The monomethylic ether, $C_6H_4(OH).CO_2CH_3$, is the chief constituent of wintergreen oil. It is a fragrant liquid of specific gravity 1.197 at 0° , boiling at $224^\circ C.$ ($435.2^\circ F.$), colored violet by ferric chloride. The monomethylic ether boils at $221^\circ C.$ ($429.8^\circ F.$).

The dimethylic ether, $C_6H_4(OCH_3).CO_2CH_3$, an oil boiling at $240^\circ C.$ ($464^\circ F.$), is formed by heating the monomethylic ether with alcoholic potash and methyl oxide:



This ether, saponified with potash, yields methyl alcohol and methylsalicylic acid, $C_6H_4(OCH_3).CO_2H$, which forms large tabular crystals, melting at $98^\circ C.$ ($208.4^\circ F.$), easily soluble in hot water and alcohol, resolved at $200^\circ C.$ ($392^\circ F.$) into CO_2 and anisol, $C_6H_5.OCH_3$.

Diethyl salicylate and ethylsalicylic acid are formed in like manner; the latter melts at $19.5^\circ C.$ ($67.1^\circ F.$), and is resolved at $300^\circ C.$ ($572^\circ F.$) into CO_2 and phenetol, $C_6H_5.O.C_2H_5$.

Acetyl salicylic acid, $C_6H_4(O.C_2H_3O).CO_2H$, formed by the action of acetyl chloride on salicylic acid, crystallizes in slender needles.

META-OXYBENZOIC ACID, $C_6H_4(OH).CO_2H$ (1 : 3), ordinary oxybenzoic acid, is formed by the action of nitrous acid on metamidobenzoic acid, and by fusing metabromo-, iodo-, or sulpho-benzoic acid with potash. It is sparingly soluble in cold water and alcohol, easily in the same liquids when hot, and separates on cooling as a crystalline powder. It melts at $200^\circ C.$ ($392^\circ F.$), sublimes undecomposed, and is altogether more stable than either of its isomerides, being resolved into CO_2 and phenol only by distillation with lime. It is not colored by ferric chloride. Its ethylic ether, $C_6H_4(OH).CO_2C_2H_5$, crystallizes in plates, dissolves in hot water, melts at $75^\circ C.$ ($161.6^\circ F.$), and boils at $280^\circ C.$ ($536^\circ F.$). The dimethylic ether, $C_6H_4(OCH_3).CO_2CH_3$, is formed by heating the acid with CH_3I and KOH to 140° , and converted by boiling with potash into methyl-oxybenzoic acid, $C_6H_4(OCH_3).CO_2H$, which crystallizes in long needles, dissolves easily in hot water, melts at 100° , and sublimes undecomposed.

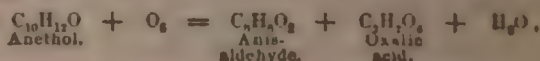
PARA-OXYBENZOIC ACID, $C_6H_4(OH).CO_2H$ (1 : 4), is formed, as above mentioned, by heating potassium phenate in a stream of carbon dioxide; also from (1 : 4) chloro-, bromo-, iodo-, and sulpho-benzoic acid, and from various resins, by fusion with potassium hydroxide; by the action of nitrous acid on paramidobenzoic acid; and by heating anisic (methyl-paraoxybenzoic) acid with strong hydriodic acid: $C_6H_3(CH_3O)_2 + HI = CH_3I + C_6H_4O_2$. It is more soluble in cold water than metaoxybenzoic or salicylic acid, dissolving in 126 parts of water at $15^\circ C.$ ($59^\circ F.$): from a hot solution it crystallizes in small distinct monoclinic prisms, containing 1 mol. H_2O . Its solution forms, with ferric chloride, a yellow precipitate insoluble in excess, without violet coloration. In the anhydrous state it melts at $210^\circ C.$ ($410^\circ F.$), with partial resolution into CO_2 and phenol.

Its basic barium salt, $C_6H_4\left<\begin{smallmatrix} O \\ CO \end{smallmatrix}\right>Ba$, is insoluble, and affords the means of separating paraoxybenzoic acid from the meta-acid.

Monomethylic paraoxybenzoate forms large tabular crystals, melts at 17° C. (62.6° F.), and boils at 283° C. (541.4° F.). The *ethyl ether* melts at 11° C. (235.4° F.), and boils at about 297° C. (566.6° F.).

Methyl-paraoxybenzoic and Ethyl-paraoxybenzoic acids are prepared in the same manner as the ortho- and meta-compounds.

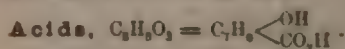
Methyl-paraoxybenzoic or *Anisic acid*, $C_8H_8(OCH_3).CO_2H$, is also produced by oxidation of anisaldehyde and anethol (p. 885)—or the crude oils of anise, fennel, and tarragon, which contain anethol—with nitric acid or chromic acid mixture. The anethol is first converted into anisaldehyde:



and the aldehyde is afterwards oxidized to anisic acid. Anisic acid is also produced by oxidation of methyl-paraeresol, $C_8H_8(OCH_3).CH_3$.

Anisic acid crystallizes from hot water in long needles, from alcohol in rhombic prisms; melts at 183° C. (361.4° F.); sublimes and boils without decomposition at 283° C. (541.4° F.). By heating with lime or baryta it is resolved into CO_2 and anisol, $C_8H_8O.CH_3$. Heated with HCl or H_2 it yields paraoxybenzoic acid. Its salts are easily soluble in water, and crystallize well.

With the halogens and with nitric acid, anisic acid readily yields substitution-products, which are converted by distillation with baryta into substituted anisols. By the successive action of fuming nitric acid and ammonia, anisic acid is converted into chrysanic acid, $C_8H_7(NO_2)_2(NH_2).CO_2H$ (p. 900).



1. **CRESOTIC** or **OXYTOLUIC** ACIDS, $C_8H_7(CH_3) \begin{array}{l} \text{OH} \\ \text{CO}_2H \end{array}$.—Three cresotic acids are formed by the action of Na and CO_2 on the three isomeric cresols (p. 869):



They crystallize in needles, dissolve in hot water, and are colored violet by ferric chloride. The acid from *o*-cresol melts at 163° – 164° C. (325.4° – 327.2° F.); that from *m*-cresol at 114° C. (237.2° F.), that from *para* at 150° C. (302° F.).

A fourth oxytoluic acid is obtained from sulphotoluic acid (from camphor-thiocyment) by fusion with potash; it melts at 203° C. (397.4° F.) and is not colored by ferric chloride.

2. **MANDLIC** or **PHENYLGLYCOLIC** ACID, $C_8H_7.CH \begin{array}{l} \text{OH} \\ \text{CO}_2H \end{array}$, is formed by boiling bitter almond oil for 30–36 hours with hydrocyanic and hydrochloric acids:



also by heating amygdalin (see Glucosides) with hydrochloric acid. It crystallizes in prisms or tables, easily soluble in water, alcohol, and ether melting at 115° C. (239° F.). By oxidizing agents it is converted into benzoic acid; by hydriodic acid into alphetolonic (phenylacetone) acid. With HBr it yields *phenylmannic* acid, $C_8H_7.CHBr.CO_2H$, and with HCl the corresponding chlorinated acid.

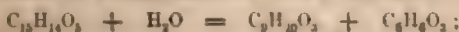
Acids, $C_9H_{10}O_2$.

1. OXYMESITYLENIC ACID, $C_9H_7(CH_3)_2\begin{smallmatrix} \text{OH} \\ \text{CO}_2\text{H} \end{smallmatrix}$, formed by heating mesitylenesulphonic acid with potash to $240^\circ\text{--}253^\circ\text{C}$. ($464^\circ\text{--}482^\circ\text{F}$.), crystallizes from alcohol in silky needles, melts at 176°C . (348.8°F .), and sublimes in long flat needles. Its solutions and those of its salts are colored dark blue by ferric chloride.

2. HYDROCOUMARIC OR MELILOTIC ACID, $C_9H_6\begin{smallmatrix} \text{OH} \\ \text{CH}_2\text{CH}_2\text{CO}_2\text{H} \end{smallmatrix}$ (1 : 2), occurs in the yellow mellilot, and is formed by the action of sodium on coumarin (p. 914) and coumaric acid: $C_9H_6O_2$ (coumarin) + H_2O + $H_2 = C_9H_{10}O_2$. It crystallizes in long needles melting at 82°C . (179.6°F .). Its solution is colored bluish by ferric chloride. By distillation it is converted into the anhydride, $C_9H_6O_2 = C_8H_4\begin{smallmatrix} \text{O} \\ \text{C}_2\text{H}_4\text{CO} \end{smallmatrix}$, which melts at 25°C . (77°F .). By fusion with potash, melilotic acid is resolved into acetic and salicylic acid, and is therefore an ortho-diderivative of benzene.

3. HYDROPARACOUMARIC ACID, $C_9H_8\begin{smallmatrix} \text{OH} \\ \text{CH}_2\text{CH}_2\text{CO}_2\text{H} \end{smallmatrix}$ (1 : 4), is produced by the action of sodium-amalgam on paracoumaric acid, and of nitrous acid on para-amidocinnamic acid. It forms small monoclinic crystals, easily soluble in water, alcohol, and ether; melting at 125°C . (257°F .). By fusion with potash it yields para-oxybenzoic acid.

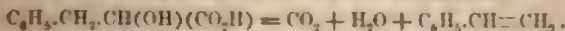
4. PHLORETIC ACID, $C_9H_8\begin{smallmatrix} \text{OH} \\ \text{CH}(\text{CH}_3)(\text{CO}_2\text{H}) \end{smallmatrix}$ (1 : 4), is formed, together with phloroglucin, by heating phloretin with potash-lye:



also by the action of sodium and CO_2 on phlorol, C_9H_9OH (p. 871). It crystallizes in long prisms, easily soluble in hot water, melting at 129°C . (264.2°F .). Ferric chloride colors its solution green. By heating with baryta it is resolved into CO_2 and phlorol; by fusion with potash into acetic and paroxybenzoic acids. *Methylphloretic acid* is converted by oxidation into anisic acid.

5. TROPIC ACID, $C_9H_8\begin{smallmatrix} \text{CH} \\ \text{CO}_2\text{H} \end{smallmatrix}\begin{smallmatrix} \text{CH}_2\text{OH} \end{smallmatrix}$, *Phenyl-hydracrylic acid*, formed from tropine by boiling with hydrochloric acid or with baryta-water, crystallizes in slender prisms melting at 117°C . (242.6°F .). By long boiling with baryta it is converted into atropic and isotropic acids (p. 533), which by oxidation yield benzoic acid. Atropic acid is therefore a monoderivative of benzene.

6. PHENYL-LACTIC ACID, $C_6H_5\text{CH}_2\text{CH}\begin{smallmatrix} \text{OH} \\ \text{CO}_2\text{H} \end{smallmatrix}$, *Phenyl-chlorolactic acid*, $C_6H_5\text{CHClCH}(\text{OH})(\text{CO}_2\text{H})$, formed by addition of $ClOH$ to cinnamic acid, $C_6H_5\text{CH}=\text{CH}\text{CO}_2\text{H}$, and phenyl-bromolactic acid, formed by boiling cinnamic dibromide, $C_6H_5\text{CHBrCHBrCO}_2\text{H}$, with water (p. 907), are both converted by sodium amalgam into phenyl-lactic acid. This acid crystallizes in concentric groups of needles, very soluble in hot water, melting at 100°C . (201.2°F .). At 180°C . (356°F .) it decomposes into water and cinnamic acid. When quickly heated it yields cinnamene:

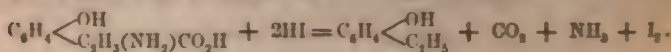


Heated with concentrated haloid acids it exchanges its hydroxyl-group for halogen elements, yielding substituted phenyl-propionic acids, e. g., $C_6H_5\text{CH}_2\text{CHBrCO}_2\text{H}$ (p. 905).

Tyrosine, $C_9H_{11}NO_3$, probably $C_6H_4\begin{smallmatrix} OH \\ \diagup \end{smallmatrix}C_2H_3(NH_2).CO_2H$, *Para-xyphenyl-amidopropionic* or *Amido-hydroparacoumaric acid*, is a compound nearly related to phloretic or hydroparacoumaric acid. It is produced, together with leucine, aspartic acid, and glutamic acid by boiling various animal substances, as albuminoids, horn, hair, etc., with hydrochloric or sulphuric acid, or by fusing them with potash. It sometimes occurs ready-formed in the liver, spleen, and pancreas; also in old cheese (*casu*). It is best prepared by boiling horn-shavings with 2 parts of sulphuric acid diluted with 4 parts of water for about 20 hours, renewing the water as it evaporates. The solution is then saturated with milk of lime, and the tyrosine is precipitated from the concentrated filtrate by acetic acid.

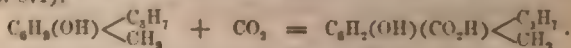
Tyrosine is insoluble in ether, slightly soluble in cold water and in alcohol, dissolves in 150 parts of hot water, and crystallizes therefrom in slender needles. It dissolves easily in hydrochloric acid, forming the salt $C_9H_{11}NO_3.HCl$, which crystallizes in needles. The aqueous solution of tyrosine boiled with mercuric nitrate yields a yellowish precipitate, which, when boiled with dilute yellow nitric acid, becomes dark red; this is a very delicate test for tyrosine. With chlorine and bromine tyrosine yields chlor- and bromanil, $C_6Cl_4O_2$ and $C_6Br_4O_2$; with nitric acid it yields substitution-products. Sulphuric acid dissolves it, forming sulpho-acids whose salts are colored violet by ferric chloride.

Tyrosine fused with potash is resolved into acetic acid, ammonia, and para-oxybenzoic acid. Heated to $140^\circ C.$ ($284^\circ F.$) with hydriodic acid, it yields phlorol (p. 871), together with CO_2 and NH_3 :



These reactions show that tyrosine is a para-derivative of benzene, containing the NH_2 -group in the lateral chain.

Acids, $C_{11}H_{14}O_3$.—Two isomeric acids, thymotic and carvacrotic, are formed by the action of sodium and CO_2 on thymol and carvacrol (p. 871):



Thymotic acid forms long needles, very slightly soluble in cold water; melts at $120^\circ C.$ ($248^\circ F.$), and sublimes. Carvacrotic acid sublimes in flat needles, melting at $134^\circ C.$ ($273.7^\circ F.$). Both are colored a fine blue by ferric chloride.

Phenylpropyl-glycollic acid, $C_6H_4\begin{smallmatrix} C_3H_7 \\ \diagup \\ CH(OH) \end{smallmatrix}.CO_2H$, formed by the action of hydrochloric and hydrocyanic acids on cuminal, crystallizes in small needles, moderately soluble in cold water, very soluble in alcohol and ether, melting at $158^\circ C.$ ($316.4^\circ F.$).

(2) UNSATURATED ACIDS, $C_nH_{2n-10}O_3$.

Coumaric and Paracoumaric Acids, $C_9H_8O_3$, $C_6H_4\begin{smallmatrix} CH \\ \diagup \\ OH \end{smallmatrix}-CH.CO.OH$, the only known acids of this series, have the composition of oxycinamic or oxyphenyl-acrylic acid.

Paracoumaric acid (1:4), produced by boiling an aqueous solution of aloes with sulphuric acid, crystallizes in colorless, shining, brittle

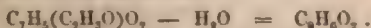
needles, easily soluble in hot water and in alcohol, melting at $170^{\circ}\text{--}180^{\circ}\text{C}$. ($335^{\circ}\text{--}355^{\circ}\text{F}$.). By nascent hydrogen it is converted into hydroparacoumaric acid; by fusion with potash, into paroxybenzoic acid.

Coumaric acid (1 : 2) occurs, together with melilotic acid (p. 930), in the yellow melilot, and in Faham leaves, and is most easily prepared from coumarin, its anhydride, by boiling with potash. It crystallizes in colorless shining prisms, easily soluble in hot water and alcohol, melting at 195°C . (383°F .). The solutions of its alkali-salts exhibit a bright green fluorescence. By nascent hydrogen it is converted into melilotic acid; by fusion with potash into salicylic and acetic acids.

Coumarin, $\text{C}_9\text{H}_6\text{O}_2$, or Coumaric anhydride,

$\text{C}_6\text{H}_5\text{--}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{--CH=CH--CO}$, is the odoriferous principle of the Tonka bean (*Dipteryx odorata*), and of several other plants, as *Melilotus officinalis*, *Asperula odorata*, and *Anthoranthum odoratum*. It may be extracted from these plants by alcohol, and crystallizes in slender, shining, colorless needles, melting at 67°C . (152.6°F .), boiling between 290°C . (554°F .) and 291°C ., and distilling without decomposition at a higher temperature. It has a fragrant odor and burning taste; is very slightly soluble in cold water, more soluble in hot water and in alcohol. It dissolves in potash-lye, and is converted by long boiling therewith into coumaric acid. Sodium-amalgam converts it into melilotic acid.

Coumarin is formed artificially by dehydration of acetosalicylal (isomeric with coumaric acid) in the manner already described (action of acetic anhydride on sodium-salicylal, p. 890):



By acting on sodium-salicylal in like manner with butyric and valeric anhydrides, homologues of coumarin are obtained, viz., butyric coumarin, $\text{C}_{11}\text{H}_{10}\text{O}_2$, and valeric coumarin, $\text{C}_{11}\text{H}_{10}\text{O}_2$. Both crystallize in prisms, the former melting at 71°C . (159.8°F .), and boiling at 297°C . (566.6°F .), the latter melting at 54°C . (129.2°F .), and distilling with partial decomposition at 300°C . (572°F .).

MONOBASIC AND TRIATOMIC ACIDS—DIOXYACIDS.

(1) **Dioxybenzoic Acids**, $\text{C}_7\text{H}_5\text{O}_4 = \text{C}_6\text{H}_3\left\{\begin{smallmatrix} (\text{OH})_2 \\ (\text{CO}_2\text{H}) \end{smallmatrix}\right.$.—Of six possible isomerides included in this formula, four are known, but the orientation of their lateral chains is not yet completely established.*

Two dioxybenzoic acids are obtained by fusing the two disulphobenzoic acids (p. 903) with potassium hydroxide. One of these dioxy-acids forms crystals containing $1\frac{1}{2}\text{H}_2\text{O}$, melts with decomposition at about 220°C . (428°F .), and is not colored by ferric chloride. The other, prepared also from toluenedisulphonic acid, forms hydrated crystals melting at 194°C . (381.2°F .), and is colored dark-red by ferric chloride.

Oxysalicylic Acid, $\text{C}_7\text{H}_5(\text{OH})_2\text{CO}_2\text{H}$ (probably 1 : 2 : 3, CO_2H in 1) is formed by boiling a solution of iodosalicylic acid, $\text{C}_7\text{H}_3\text{IO}_3$, with potash. It crystallizes in shining needles, soluble in water, alcohol, and ether. The aqueous solution, mixed with ferric chloride, acquires a deep-blue

* See Watts's Dictionary of Chemistry, 2d Supplement, p. 432.

color, changing to red and then brown on addition of ammonia or sodium carbonate. The crystallized acid melts at $196-197^{\circ}\text{C}$. ($384.8-389^{\circ}\text{F}$.), and is resolved at a higher temperature into CO_2 and hydroquinone (together with pyrocatechin). The oxy-salicylates are very unstable.

Protocatechuic Acid, $\text{C}_6\text{H}_3(\text{OH})_2(\text{CO}_2\text{H})$ (probably 1 : 3 : 4, CO_2H is 1), also called *Carbolydroquinone acid*.—This acid is produced by the action of melting potash on its aldehyde, and on isoparaoxybenzene, bromoparacresolsulphonic, and eugenic acids, catechin, and many other tri-derivatives of benzene; also on numerous resins, as benzoin, myrrh, dragon's blood, assafetida, etc., its formation from these resins being usually accompanied by that of paraoxybenzoic acid. It is also formed by the action of bromine on aqueous quinic acid, and by fusing that acid with potash. It is most easily prepared by adding 1 part of East Indian kino to 3 parts of fused sodium hydroxide, dissolving the melt in water, acidulating, and agitating with ether.

Protocatechuic acid crystallizes from water in shining needles or lamæ containing 1 mol. H_2O . It dissolves easily in hot water, in alcohol, and in ether, and in 40–50 parts of cold water; melts at 199°C . (390.2°F .), and decomposes at a higher temperature into CO_2 and pyrocatechin (together with hydroquinone). Ferric chloride colors the solution green, changing, on addition of very dilute sodium carbonate, to blue and afterwards to red. It reduces silver nitrate, but not an alkaline cuprous solution.

Methyl-protocatechuic or Vanillic acid, $\text{C}_8\text{H}_7\text{O}_4 = \text{C}_6\text{H}_3(\text{OH})_2(\text{OCH}_3)(\text{CO}_2\text{H})$, is formed by oxidation of vanillin (p. 891), when that substance, in the moist state, is left exposed to the air, and by oxidation of coniferin, $\text{C}_{16}\text{H}_{22}\text{O}_8$ (see GLUCOSIDES) with potassium permanganate. It crystallizes in shining white needles, melting at $211^{\circ}-212^{\circ}\text{C}$. ($411.8-413.6^{\circ}\text{F}$.); sublimable; sparingly soluble in cold water, easily in hot water and in alcohol, decomposed by hydrochloric acid at 100°C . ($302^{\circ}-320^{\circ}\text{F}$

An isomeric methyl-protocatechuic acid is formed by heating protocatechuic acid with potassium hydroxide and methyl iodide, also by heating hemipinic acid with strong hydrochloric acid at 100°C . It crystallizes in slender needles, less soluble than the preceding, and melting at 207°C . (403.8°F .).

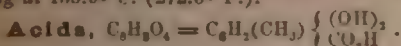
Dimethyl-protocatechuic or Veratric acid, $\text{C}_8\text{H}_7\text{O}_4 = \text{C}_6\text{H}_3(\text{OCH}_3)_2(\text{CO}_2\text{H})$, is contained in sanddilla seeds (from *Veratrum Sabadilla*), and is formed by heating protocatechuic or methyl-protocatechuic acid with KHO , methyl iodide and methyl alcohol to 140°C . (284°F .), and boiling the product with soda-lye; also by oxidation of dimethyl-protocatechuic aldehyde (p. 891), methyl-cresol (p. 800), and methyl-eugenol (p. 886), with permanganate. Colorless needles melting at 179°C . (355.1°F .), slightly soluble in cold water, more easily in hot water, and more in alcohol. Heated to $140^{\circ}-150^{\circ}\text{C}$. ($284^{\circ}-302^{\circ}\text{F}\text{CO}_2$ and dimethyl-pyrocatechin.

In like manner are obtained: *Diethyl-protocatechuic acid* (needles, m. p. 149°C . (300.2°F .)), and *Ethyl-methyl-protocatechuic or Ethyl-vanillic acid* (needles slightly soluble in hot water; m. p. 132°C . (274°F .)),

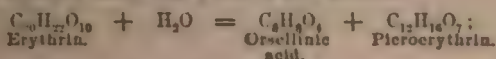
Methylene-protocatechuic or Piperonglic acid, $\text{C}_8\text{H}_6\text{O}_4 = \text{CH}_2 \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{C}_6\text{H}_3(\text{OH})_2(\text{CO}_2\text{H})$, is formed by oxidation of its aldehyde, piperonglic

$C_8H_6O_2$ (p. 891), with permanganate, and by heating protocathechuic acid with KOH and CH_3I .—Colorless needles, m. p. $228^\circ C.$ ($442^\circ F.$), sublimable without decomposition, insoluble in cold water, slightly soluble in boiling water and cold alcohol, easily in hot alcohol. Decomposed by heating to $170^\circ C.$ ($338^\circ F.$) with dilute hydrochloric acid into protocathechuic acid and free carbon; by heating with water to $200-210^\circ C.$ ($392-410^\circ F.$), into pyrocatechin, CO_2 , and carbon.

Ethene-protocatechuic acid, $C_8H_8O_4$, obtained by heating protocathechuic acid with KOH, C_2H_5Br , and a little water to 100° , forms shining prisms melting at $133.5^\circ C.$ ($272.3^\circ F.$).



Orsellinic Acid is formed by boiling orsellin or lecanoric acid with lime-water: $C_{16}H_{14}O_7 + H_2O = 2C_8H_8O_4$; also by boiling its erythritic ether (erythrin or erythric acid) with water or baryta-water:

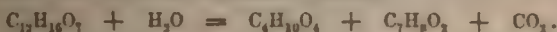


Orsellinic acid crystallizes in prisms easily soluble in water, colored violet by ferric chloride. It melts at $176^\circ C.$ ($348.8^\circ F.$), decomposing at the same time into CO_2 and orein, $C_7H_8O_2$ (p. 876).

Ethyl Orsellinate, $C_8H_7(CH_3)(OH)_2.CO_2.C_2H_5$, is obtained by boiling orsellinic acid, or *Rocella tinctoria*, with alcohol. It crystallizes in lustrous plates easily soluble in boiling water, alcohol, and ether.

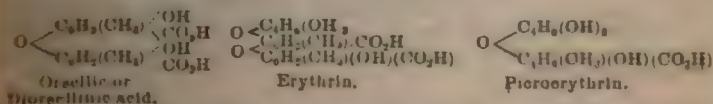
Erythritic Orsellinate, Erythrin or Erythric acid, $C_{30}H_{22}O_{10} = 2C_8H_8O_4 + C_4H_{10}O_4$ (erythrite) $- 2H_2O$, is contained in *Rocella fusiformis*, and extracted by boiling with milk of lime. It forms crystals containing $\frac{1}{2} H_2O$, slightly soluble in hot water, colored red by ammonia in contact with air, and is resolved by boiling with baryta-water into orsellinic acid and picroerythrin (see above).

Picroerythrin, $C_{12}H_{16}O_7$, forms crystals containing 1 mol. H_2O , soluble in alcohol and ether, and is resolved by further boiling with baryta-water into erythrite, orein, and carbon dioxide:



Orsellin, *Lecanoric*, or *Diorsellinic acid*, $C_{16}H_{14}O_7 = 2C_8H_8O_4 - H_2O$, occurs in several lichens belonging to the genera *Rocella*, *Lecanora*, and *Variolaria*, and is extracted by digestion with ether or with milk of lime, and precipitation by hydrochloric acid. It crystallizes from alcohol or ether in colorless prisms containing $C_{16}H_{14}O_7 + H_2O$, nearly insoluble in water. By boiling with lime or baryta-water it is converted, first into orsellinic acid, afterwards into CO_2 and orein. Its alcoholic solution yields, on boiling, crystalline ethyl orsellinate.

The three compounds last described may be represented by the following structural formulae:



According to Stanhouse,* the South African variety of *Rocella tinctoria* contains an acid, $C_{34}H_{22}O_{15}$, called β -orsellinic acid, closely resembling orsellinic

acid in properties and composition, and yielding orsellinic acid when boiled with baryta-water, together with roscellinin, $C_{15}H_{10}O_7$, a substance forming hair-like crystals of a silvery lustre: $C_{15}H_{10}O_7 = 2C_7H_6O_4 + C_{15}H_{10}O_7$. Roscellinin is not attacked by boiling with potash or baryta. It dissolves in ammonia and the fixed alkalis, forming solutions which are not colored by exposure to the air.

The following acids of unknown structure are also obtained from lichens:

Vulpic acid, $C_{15}H_{14}O_8$, occurs in *Cetraria vulpina*, from which it may be extracted by chloroform or lime-water. It forms large yellow prisms, slightly soluble in water and in ether, melts at 110°C . (230°F .), sublimes without decomposition, and is resolved by boiling with baryta-water into alphetolufic acid, methyl alcohol, and oxalic acid.

Usnic acid, $C_{15}H_{10}O_7$, from lichens of the genera *Usnea* and *Evernia*, crystallizes in shining yellow laminae, insoluble in water, slightly soluble in alcohol and ether, melting at $195^\circ\text{--}197^\circ\text{C}$. ($383^\circ\text{--}386.6^\circ\text{F}$.). Its alkali-salts, when exposed to the air, turn red and afterwards black. A modification, called **Beta-usnic acid**, from *Cladonia rangiferina*, melts at 175°C . (347°F .), and yields by distillation beta-orcin (p. 877).

Cetraric acid, $C_{15}H_{10}O_8$, and **Lichenic acid**, $C_{14}H_{10}O_8$, from Iceland moss (*Cetraria islandica*), are crystalline, and easily soluble in alcohol and ether.

Acids, $C_9H_8O_4 = C_9H_7(OH)_2.CO_2H$:

Evernic Acid is obtained from evernic acid, $C_{17}H_{12}O_7$ (a constituent of *Evernia Prunastri*), by boiling with baryta:



It crystallizes from hot water in needles, melts at 157°C . (314.6°F .), and is colored violet by ferric chloride.

Umbellic Acid is formed by the action of sodium-amalgam on umbelliferone: $C_9H_6O_3 + H_2O + H_2 = C_9H_8O_4$. It crystallizes in colorless needles, melting at 125°C . (257°F .), slightly soluble in water, easily in alcohol and ether. With ferric chloride it produces a green color, turning red on addition of sodium carbonate. Fused with potash it yields resorcin.

Umbelliferone, $C_9H_6O_3$, a compound analogous to coumarin (p. 914), occurs in the bark of *Daphne Mezereum*, and is produced by distillation of galbanum, assafoetida, and other resins of umbelliferous plants. It crystallizes from hot water in rhombic prisms, slightly soluble in cold water, easily in hot water and in alcohol; its aqueous solution appears blue by reflected light. It melts at 240°C . (464°F .), and sublimes without decomposition; yields resorcin by fusion with potash, and is converted by sodium-amalgam into umbellic acid, just as coumarin is converted into hydrocoumaric acid.

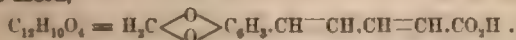
Hydrocaffeic Acid, $C_8H_7(OH)_2-CH_2-CH_2-CO_2H$, formed by the action of sodium-amalgam on caffeic acid, forms crystals easily soluble in water, and is colored dark-green by ferric chloride,

The following unsaturated acids belong to the triatomic and monobasic division.

Caffeic Acid, $C_8H_8O_4 = C_6H_3(OH)_2-CH=CH-CO_2H$, formed by boiling caffeotannic acid (p. 921) with potash, crystallizes in yellowish prisms, very soluble in hot water and alcohol. The aqueous solution reduces silver nitrate when heated. Ferric chloride colors it green, changing to dark red on addition of sodium carbonate. By fusion with potash caffeic acid is resolved into protocatechuic and acetic acids. By dry distillation it yields pyrocatechin. Sodium-amalgam converts it into hydrocaffeic acid.

Ferulic Acid, $C_{10}H_{10}O_4 = C_6H_3(OH)_2-C_3H_4-CO_2H$, occurs in assafoetida, and may be separated from the alcoholic extract of that substance by precipitating with lead acetate, and decomposing the precipitate with sulphuric acid. It dissolves easily in hot water and alcohol, and crystallizes in four-sided needles. Its aqueous solution is colored yellow-brown by ferric chloride. By fusion with potash it is resolved into protocatechuic and acetic acids.

Piperic Acid,



The potassium salt of this acid is obtained by boiling piperine (*q. v.*) with alcoholic potash, and separates in shining prisms. The free acid crystallizes in slender needles melting at $216^\circ-217^\circ$ C. ($420.8^\circ-422.6^\circ$ F.). It forms sparingly soluble salts containing 1 equivalent of base. It unites with 4 atoms of bromine, and is resolved by fusion with potash into acetic, oxalic, and protocatechuic acids. By oxidation with permanganate solution it yields piperonal (p. 891).

Eugetic Acid, $C_{11}H_{12}O_4 = C_6H_3(OH)(OCH_2) \begin{array}{c} \diagup CO_2H \\ \diagdown CH-CH_2 \end{array}$, is formed by the action of sodium and carbon dioxide on eugenol, $C_{10}H_{12}O_2$ (p. 885). It crystallizes in thin prisms, slightly soluble in water, melts at 124° C. (255.2° F.), and is resolved at a higher temperature into CO_2 and eugenol. Ferric chloride colors its solution dark brown.

MONOBASIC AND TETRATOMIC ACIDS.

Gallie Acid, $C_7H_6O_5 = C_6H_2(OH)_3-CO_2H$ —*Trioxylbenzoic acid*, *Dioxy-salicylic acid*.—This acid occurs in nut-galls (excrecences formed on the leaves and leaf-stalks of the dyer's oak (*Quercus infectoria*), also in sumach, hellebore root, divi-divi (the fruit of *Glaspina coriaria*), in tea, in pomegranate root, and in many other plants. It is produced artificially by heating di-iodosalicylic acid to $140^\circ-150^\circ$ C. ($284^\circ-302^\circ$ F.), with excess of an alkaline carbonate; and from bromodioxybenzoic acid and bromo-protocatechuic acid (p. 916) by fusion with potash: hence its structure is either 1 : 2 : 3 : 4 or 1 : 2 : 4 : 5 (CO_2H in 1). It is most conveniently prepared by boiling gallotannic acid with acids or alkalis: $C_{16}H_{10}O_9 + H_2O = 2C_7H_6O_5$.

Gallie acid crystallizes, with 1 mol. H_2O , in slender prisms having a silky lustre; dissolves in 100 parts of cold and 3 parts of boiling water, easily in alcohol; melts at about 200° , and splits up at $210^\circ-220^\circ$ C. ($410^\circ-428^\circ$ F.) into CO_2 and pyrogallol, $C_6H_3(OH)_3$. The aqueous solution reduces the metals from solutions of gold and silver salts (hence its

use in photography), and forms a blue-black precipitate with ferric chloride.

Gallie acid, though monobasic, contains 3 atoms of phenolic hydrogen, and can therefore form tetrametallic salts. The gallates of the alkali-metals are permanent in the dry state and in acid solution, but in alkaline solution they quickly absorb oxygen and turn brown.

Ethyl gallate, $C_6H_2(OH)_3 \cdot CO_2C_2H_5$, crystallizes from water in rhombic prisms containing $\frac{2}{3}$ mol. H_2O . *Triacetyl-gallie acid*, $C_6H_2(OC_2H_3O)_3 \cdot 3C_2H_5$, formed by heating gallie acid with acetyl chloride or acetic anhydride, crystallizes from alcohol in needles. With bromine gallie acid forms $C_7H_2BrO_6$ and $C_7H_4Br_2O_6$, both of which are crystalline.

Gallie acid, heated with 4 parts of sulphuric acid to 140° , is converted into rufigallie acid, $C_{14}H_8O_6$, a derivative of anthracene.

Ellagic acid, $C_{10}H_6O_6$, probably also an anthracene derivative, is formed by the action of oxidizing agents—as arsenic acid, silver oxide, iodine and water—on gallie acid; also from tannic acid when its concentrated aqueous solution is left for a considerable time in contact with the air, the ellagic acid then separating, together with gallie acid. It is a constituent of bezoar stones (intestinal concretions of a Persian species of goat), from which it may be obtained by boiling with potash and precipitating with hydrochloric acid. It separates, with 1 mol. H_2O , as a crystalline powder, insoluble in water, and having an acid reaction. Its sodium salt is formed by boiling ethyl gallate with sodium carbonate.

Tannic Acids or Tannins.

These substances constitute the astringent principles of plants, and are very widely diffused in the vegetable kingdom. Most of them are glucosides of gallie acid, being resolved by boiling with dilute acids into gallie acid and glucose; others, instead of glucose, yield phloroglucin, $C_6H_2(OH)_3$, (p. 878). Gallotannic acid, on the other hand, when quite pure, is not a glucoside, but consists of digallie acid. By fusion with potash most tannic acids are resolved into protocathechuic acid and phloroglucin.

Most tannic acids give bluish-black precipitates with ferric salts (inks); some, however, as kino and catechu, and the tannins of sumach and of the tea-plant, give greenish precipitates. The tannic acids precipitate a solution of gelatin, and unite with animal membranes: hence their use in the manufacture of leather. They are precipitated from their solutions by neutral acetate of lead.

Gallotannic Acid, Digallie Acid or Tannin, $C_{14}H_{10}O_6 = C_6H_2(OH)_3 - CO - O - CO - C_6H_2(OH)_3$, occurs in large quantity in nut-galls, especially in the Chinese variety, also in sumach (the twigs of *Rhus Coriaria*), in tea, and many other plants. It may be formed from gallie acid by heating with $POCl_3$ to $120^\circ C.$ ($248^\circ F.$), and by oxidation with silver nitrate or dilute arsenic acid. It is most readily prepared by exhausting finely pulverized nut-galls with a mixture of alcohol and ether in a percolator (fig. 177), having its neck plugged with cotton-wool, and its mouth loosely stopped with a cork. The liquid, which after some time collects in the receiver below, consists of two distinct strata: the lower, which is almost colorless, is a very strong solution of almost pure tannic acid in water; the upper consists of ether, holding in solution gallie acid, coloring matter, and other impurities. The carefully separated heavy liquid is left to evaporate in an exsiccator. Gallotannic acid, or *tannin*, thus obtained, forms a slightly yellowish, friable, porous mass, without the slightest

tendency to crystallization. It is very soluble in water, less so in alcohol, and very slightly soluble in ether. It reddens litmus, and has a pure astringent taste without bitterness.

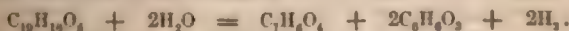
A strong solution of gallotannic acid mixed with mineral acids gives precipitates consisting of combinations of the tannic acid with the mineral acids; these compounds are freely soluble in pure water, but nearly insoluble in acid liquids. Gallotannic acid precipitates albumin, gelatin, salts of the vegetable-alkalies, and several other substances: it forms soluble compounds with the alkalies, which, if excess of base is present, rapidly attract oxygen, and become brown by destruction of the acid; the gallotannates of barium, strontium, and calcium are sparingly soluble; those of lead and antimony are insoluble. Ferrous salts are unchanged by solution of gallotannic acid; ferric salts, on the contrary, give with it a deep bluish-black precipitate, which is the basis of writing-ink: hence the value of an infusion of tincture of nut-galls as a test for the presence of iron.

Gallotannic acid decomposes at 250°C . (482°F .), with formation of pyrogallol. By boiling with alkalies or dilute acids it is converted into gallic acid, $\text{C}_{14}\text{H}_{10}\text{O}_9 + \text{H}_2\text{O} = 2\text{C}_6\text{H}_4\text{O}_5$; hence its constitution is determined. By boiling with excess of acetic anhydride it is converted into pentacetyl-tannic acid, $\text{C}_{16}\text{H}_2(\text{C}_2\text{H}_3\text{O})_5\text{O}_9$, a crystalline substance, melting at 137°C . (278.6°F .).

The following tannins, which are amorphous bodies, more or less resembling gallotannic acid, have not been obtained in the pure state.

Quercitannic acid, from oak-bark, is a yellow-brown amorphous mass, the aqueous solution of which is colored deep blue by ferric chloride. *Cinchonatanic acid*, occurring in cinchona barks, partly in combination with alkaloids, gives a green color with ferric salts. *Ratanhia-tannic acid* occurs in rhatany-root; *filittannic acid* in fern-roots; *tormentil-tannic acid* in tormentil-root. These five tannins, when boiled with dilute acids, yield red amorphous bodies (oak-red, cinchona-red, etc.), which partly also occur ready-formed in the respective plants, and are resolved by fusion with potash into protocatechuic acid and phloroglucin. The formation of these red compounds appears to be accompanied by that of sugar.

Catechu-tannic acid occurs in catechu, an extract prepared from several East Indian plants, viz., *Areca Catechu*, *Acacia (Mimos) Catechu*, and *Nauclaea Gambir*. Ferric salts color it dingy green. Catechu also contains catechin or catechuic acid, $\text{C}_{15}\text{H}_{10}\text{O}_8$, which crystallizes in needles containing $3\text{H}_2\text{O}$. Its aqueous solution is colored green by ferric salts. Anhydrous catechin melts at 217°C . (422.6°F .), decomposing at the same time into CO_2 and pyrocatechin. By fusion with potash it is resolved into protocatechuic acid and phloroglucin:



Morintannic acid or *Maclurin*, occurring in fustic (the wood of *Morus tinctoria*), is a yellow crystalline powder, easily soluble in hot water and in alcohol, the solutions giving with ferric chloride a greenish-black precipitate. It yields pyrocatechin when heated, phloroglucin and protocatechuic acid when fused with potash.

Coffetannic acid, from coffee-berries, is a gummy, easily soluble mass, which gives a green reaction with ferric chloride, yields pyrocatechin when

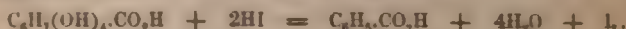
Fig. 177.



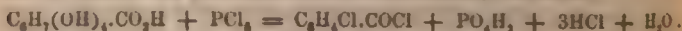
heated alone, caffeic acid (p. 919), when heated with potash-solution; protocatechuic acid when fused with potash.

Quinic or Kinic Acid, $C_7H_{12}O_6 = C_6H_7(OH)_4(CO_2H)$, is a monobasic pentatonic acid, nearly related to the aromatic oxy-acids. It is found in cinchona-bark, and is obtained as a bye-product in the preparation of quinine. The extract, obtained by digesting the comminuted bark with water or dilute sulphuric acid, is mixed with milk of lime to precipitate the alkaloid; the solution is filtered and evaporated; and the calcium quininate which remains is purified by crystallization, and decomposed with oxalic acid.

Quinic acid forms transparent colorless monoclinic prisms, easily soluble in water, very slightly soluble in alcohol. It melts at $162^\circ C.$ ($323.6^\circ F.$), and at a higher temperature is resolved into hydroquinone, pyrocatechin, benzoic acid, phenol, and other products. By oxidizing agents (MnO_2 and sulphuric acid) it is converted into quinone, together with carbonic and formic acids. By heating with hydriodic acid it is converted into benzoic acid:



and by phosphorus pentachloride into chlorobenzoyl chloride:



By fusion with potash it yields protocatechuic acid.

Calcium quinate, $(C_7H_{11}O_6)_2Ca + 10H_2O$, forms large, easily soluble, efflorescent rhombic prisms.

Uvic Acid, $C_7H_6O_5$, obtained by distillation of pyrotartaric acid, forms shining crystals melting at $134^\circ C.$ ($273.2^\circ F.$) and sublimable converted into benzoic acid by fusion with potash. Its calcium-salt, $(C_7H_5O_5)_2Ca + 6H_2O$, crystallizes in needles.

Aldehydic Acids.

These are acids containing the group CHO as well as $CO.OH$, in place of hydrogen, and exhibiting an aldehydic as well as an acid character. All the known aldehydic acids likewise contain the group OH , and are therefore the intermediate aldehydes of bibasic triatomic acids. They are produced, like salicylic aldehyde (p. 885), by the action of chloroform on the oxy-acids in alkaline solution.

Aldehyde-oxybenzoic Acid, $C_8H_6O_4 = C_6H_4(OH) \begin{smallmatrix} CHO \\ CO_2H \end{smallmatrix}$. — Two isomeric acids of this composition (α and β Aldehydosalicylic acids) are obtained by boiling 14 parts of salicylic acids, 25 parts of sodium hydroxide, 50 parts of water, and 15 of chloroform, in a vessel with reversed condenser. On diluting with water, acidulating with hydrochloric acid, agitating with ether, and then agitating the concentrated ethereal solution with acid sodium sulphite, a solution is obtained, from which, after removal of the ether, sulphuric acid separates the β -acid as a crystalline powder, while the α -acid, together with a very small quantity of the β -acid, remains dissolved, and may be extracted from the solution by ether. A third acid, γ -aldehydoparaoxybenzoic acid, is obtained in like manner from paraoxybenzoic acid, together with paraoxybenzoic aldehyde.

1. ($\text{CO}_2\text{H} : \text{OH} : \text{CHO} = 1 : 2 : 3$).—Slender felted needles, sublimable when slowly heated. Much more soluble in water than 2. Solution colored by ferric chloride. Calcium-salt easily soluble; distilled with calcium carbonate gives salicylic aldehyde.

2. ($\text{CO}_2\text{H} : \text{OH} : \text{CHO} = 1 : 2 : 5$).—Slender needles melting at 249°C . (50.2°F .), sublimable when slowly heated. Nearly insoluble in cold water, sparingly soluble in boiling water and cold alcohol, easily in hot alcohol and ether. Deep cherry-red with ferric chloride. Calcium-salt easily soluble; distilled with CaH_2O_2 gives paraoxybenzaldehyde.

3. ($\text{CO}_2\text{H} : \text{OH} : \text{CHO} = 1 : 3 : 4$).—Prismatic crystals, melting at $243^\circ\text{--}245^\circ \text{C}$. ($469.4^\circ\text{--}471.2^\circ \text{F}$.), sublimable. Slightly soluble in cold, more freely in hot water, easily in alcohol and ether. Brick-red with ferric chloride. Calcium-salt slightly soluble; distilled with lime gives salicylic aldehyde.

Aldehydovanillic, or Aldehydo-methylprotocatechuic Acid,

$\text{H}_2\text{O}_2 = \text{C}_6\text{H}_3(\text{OH})(\text{OCH}_3) \begin{smallmatrix} \text{CHO} \\ \text{CO}_2\text{H} \end{smallmatrix}$, is obtained, together with vanillin (p. 891), from vanillic acid, in the same manner as the aldehydoxybenzoic acids from the oxybenzoic acids. Crystallizes in slender silky needles, melting at $221^\circ\text{--}222^\circ \text{C}$. ($429.8^\circ\text{--}431.6^\circ \text{F}$.), slightly soluble in water, freely in alcohol and ether. Ferric chloride colors the solution violet.

Opianic Acid, $\text{C}_{10}\text{H}_{10}\text{O}_5 = \text{C}_6\text{H}_3(\text{OCH}_3)_2 \begin{smallmatrix} \text{CHO} \\ \text{CO}_2\text{H} \end{smallmatrix}$.—Aldehydo-dimethylprotocatechuic acid is formed, together with cotarnine and hemipinic acid (p. 926), in the oxidation of narcotine by MnO_2 and sulphuric acid, or in dilute nitric acid. It crystallizes in slender, colorless prisms, melting at 146°C . (284°F .), slightly soluble in cold water. Heated with lime, it is converted into dimethyl-protocatechuic aldehyde, $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{CHO}$ (p. 891), and when treated with oxidizing agents, it yields hemipinic acid.

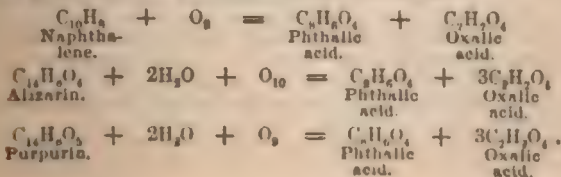
Meconin, $\text{C}_{16}\text{H}_{10}\text{O}_4$, occurs in opium, and is formed, together with tarnine (see ALKALOIDS), from narcotine, by heating with water to 100°C , and from opianic acid by the action of nascent hydrogen or of potash. Shining colorless crystals, sparingly soluble in cold, more freely in hot water, melting at 116°C . (230°F .). Heated with acids, it forms fereal compounds, with elimination of water.

BIBASIC AND DIATOMIC ACIDS.

Benzene-dicarboxylic Acids.

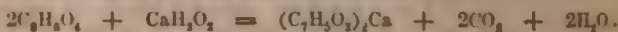
Acids, $\text{C}_6\text{H}_4\text{O}_4 = \text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$.

1. **Phthalic Acid** (1 : 2).—Orthobenzene-dicarboxylic acid is formed by the action of nitric acid on naphthalene, dichloride of naphthalene, alizarin, and purpurin (the coloring-matters of madder):



It is also produced by oxidizing orthotoluic acid with permanganate solution, and is usually prepared by treating naphthalene dichloride at the boiling heat with nitric acid. Chromic acid mixture cannot be used in its preparation, as it is easily oxidized thereby to carbonic acid.

Phthalic acid crystallizes in short prisms or laminae, slightly soluble in cold water, easily soluble in hot water, alcohol, and ether. It melts at 185°C . (365°F .), and is resolved at a higher temperature into water and phthalic anhydride, $\text{C}_8\text{H}_4\text{O}_3$. Heated with excess of calcium hydrate, it is resolved into 2CO_2 and benzene, but when 2 molecules of it are heated with 1 mol. CaH_2O_2 , it yields calcium benzoate:



It forms both acid and neutral salts. Barium chloride added to the solution of its ammonium salt throws down barium phthalate, $\text{C}_8\text{H}_4\text{O}_4\text{Ba}$, which is very slightly soluble in water.

Phthalic acid is converted by fuming nitric acid into nitro-phthalic acid, $\text{C}_8\text{H}_3(\text{NO}_2)\text{O}_4$.

Phthalic chloride, $\text{C}_8\text{H}_4(\text{COCl})_2$, formed by heating the acid with PCl_5 , is a liquid which boils at 270°C . (518°F .), and is converted by zinc and hydrochloric acid into phthalic aldehyde, $\text{C}_8\text{H}_4(\text{CHO})_2$, which crystallizes from hot water in plates, and melts at 65°C . (149°F .).

Phthalic anhydride, $\text{C}_8\text{H}_4\left\langle\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\right\rangle\text{O}$, obtained by heating the acid, forms large needles, melts at 128°C . (262.4°F .), and boils at 277°C . (530.6°F .).

Hydrophthalic acid, $\text{C}_8\text{H}_6\text{O}_4$, formed by the action of sodium-amalgam on phthalic acid, dissolved in aqueous sodium carbonate, crystallizes in tables; dissolves easily in hot water and alcohol; and melts at about 200°C . (392°F .), decomposing at the same time into phthalic anhydride, water, and hydrogen. By the action of strong sulphuric acid, or by oxidation with nitric acid, chromic acid, or bromine and water, it is converted into benzoic acid. Tetrahydrophthalic acid, $\text{C}_{10}\text{H}_{10}\text{O}_4$, is prepared by heating its anhydride with water, and the anhydride, $\text{C}_8\text{H}_4\text{O}_3$, is produced by distillation of isohydropyromellitic acid (p. 927). The anhydride crystallizes in laminae melting at 68°C . (154.4°F .). The acid also crystallizes in laminae, melting at 96°C . (204.8°F .), and decomposing at the same time into water and the anhydride. Hexahydrophthalic acid, $\text{C}_8\text{H}_{12}\text{O}_4$, is obtained from either of the preceding by the action of sodium-amalgam, or by heating with hydriodic acid to 230°C . (446°F .); it crystallizes in prisms or laminae, sparingly soluble in water, melting at 207°C . (404.6°F .).

Isophthalic Acid, $\text{C}_8\text{H}_6(\text{CO}_2\text{H})_2$ (1:3), is formed by oxidation of meta-xylene or metatoluic acid with chromic acid mixture, also by fusing meta-sulphobenzoate, or metabromobenzoate, or benzoate of potassium with potassium formate (in the last two cases together with terephthalic acid), and by the action of heat on hydropyromellitic and hydropyrenitic acid (p. 927). It crystallizes in slender needles, soluble in 460 parts of boiling and 7800 parts of cold water, melts above 300°C . (572°F .), and sublimes in needles without blackening. Its barium salt dissolves easily in water, so that the acid is not precipitated by barium chloride from the solution of its ammonium salt, a character by which it is distinguished from its two isomerides.

Methyl isophthalate, $\text{C}_8\text{H}_7(\text{CO}_2\text{CH}_3)_2$, crystallizes in needles, melting at

o C. (147.2°–149° F.). The *ethylic ether* is a colorless liquid, boiling at 54.5° C. (545° F.), and not solidifying at 0°.

isophthalic acid, $C_6H_4(NO_2)_2$, forms laminae, melting at 249° C. (480° F.).

thiyl chloride, $C_6H_4(COCl)_2$, forms a radio-crystalline mass, melts at 105.8° C. (222.4° F.), boils at 276° C. (528.8° F.).

phthalic Acid, $C_6H_4(CO_2H)_2$ (1 : 4), is formed by oxidation of bodies belonging to the para-series—as paraxylene, paratoic acid, and cymene, with chromic acid mixture. It is a white powder, fine if slowly deposited from solution, nearly insoluble in water, and ether; sublines undecomposed without previous fusion.

isophthalates, $C_6H_4O_4Ca + 3H_2O$ and $C_6H_4O_4Ba + 4H_2O$, are crystallized very sparingly soluble. The methylic and ethylic ethers crystallize in prisms, the former melting at 104° C. (219.2° F.), the latter at 111.2° C.

terephthalic acid is crystalline, and melts at 259° C. (496.2° F.).

isophthalic acid, $C_6H_4O_4$, is a white powder, like terephthalic acid.

acids, $C_9H_8O_4 = C_6H_3(CH_3)(CO_2H)_2$.

ic Acid ($CO_2H : CH_3 : CO_2H = 1 : 3 : 5$) is produced, together with **enic acid**, by prolonged boiling of mesitylene with dilute nitric acid by boiling pyruvic acid (p. 757) with barium hydrate. Slender needles, melting at 267° C. (548.6° F.), sparingly soluble in hot water, in alcohol and ether; converted by oxidation with chromic acid into **ic acid**, and resolved by distillation with lime, first into CO_2 and **ic acid**, afterwards into CO_2 and toluene.

ic Acid ($CO_2H : CH_3 : CO_2H = 1 : 3 : 4$) is produced from psene (p. 819), xylic acid, and paraxylic acid (p. 817), by prolonged boiling with dilute nitric acid. Indistinct colorless crystals, melting at 33° C. (536°–541.4° F.), nearly insoluble in cold water.

ylidic acid, formed by fusing potassium toluene-disulphonate with formate, is very much like xylidic acid, but melts at 310°–320° (590°–599° F.).

avitic acid, formed together with phloroglucin, pyrotartaric acid and acetic acid, by fusing gamboge with potash, crystallizes in short prisms, melting at about 160° C. (320° F.).

acids, $C_{10}H_{10}O_4$.

idic acid, $C_8H_4(CH_3)_2(CO_2H)_2$, formed from durene and durylic acid, by prolonged boiling with dilute nitric acid, crystallizes in long transprisms, and sublines at a high temperature.

ylene-diacetic acid, $C_6H_4(CH_2CO_2H)_2$, is formed from tolylchloride, $C_6H_4(CH_2Cl)_2$ (p. 828). Long needles, melting at 244° C. (471° F.), and subliming.

BIBASIC AND TRIATOMIC ACIDS.

oldicarbonic Acid, $C_6H_4O_5 = C_6H_3(OH)(CO_2H)_2$, is formed, together with phenol and phenoltricarboxylic acid, when basic sodium salicylate is heated to 360°–380° C. (680°–716° F.) for several hours, with agitation, in a stream of carbon dioxide. The product is dissolved

in water, acidulated with hydrochloric acid, boiled, filtered hot, neutralized with ammonia and mixed with barium chloride, whereby barium phenoldicarbonate is precipitated. The liquid filtered after cooling and mixed with hydrochloric acid, deposits a mixture of phenoldicarbonic and cyclic acids, from which the latter may be dissolved out by chloroform. Phenoldicarbonic acid crystallizes from boiling water in long needles, melts above 270°C . (516°F .), and sublimes at 200°C . (392°F .), with partial resolution into CO_2 and phenol. Slightly soluble in water, easily in alcohol and ether.

Oxysouvitic Acid, $\text{C}_6\text{H}_6\text{O}_5 = \text{C}_6\text{H}_2(\text{OH})(\text{CH}_2)(\text{CO}_2\text{H})_2$.—The ethylic ether of this acid is formed by the action of chloroform, chloral, *earles* tetrachloride or ethyl trichloracetate on ethyl acetacetate (p. 722). The free acid forms needles, sparingly soluble in cold water, more freely in hot water, easily in alcohol and ether. Ferric chloride colors its solution reddish violet. The barium salt, $\text{C}_6\text{H}_6\text{O}_5\text{Ba} + 1\frac{1}{2}\text{H}_2\text{O}$, heated with lime, yields metacresol. By oxidation with permanganate or dilute nitric acid, oxysouvitic acid is converted into an acid isomeric with uvic acid (p. 925). It is insoluble in chloroform.

Hemipinic Acid, $\text{C}_{10}\text{H}_{10}\text{O}_6 = \text{C}_6\text{H}_7(\text{OCH}_3)_2(\text{CO}_2\text{H})_2$, formed, together with cotarnine, mesonin, and opianic acid, by oxidation of narceine, crystallizes in large hydrated prisms slightly soluble in water. The dehydrated acid melts at 180°C . (356°F .). By heating with HI , it is resolved into CO_2 , methyl iodide, and protocatecholic acid: $\text{C}_{10}\text{H}_{10}\text{O}_6 + 2\text{HI} = \text{C}_7\text{H}_6\text{O}_4 + 2\text{CH}_3\text{I} + \text{CO}_2$.

TRIBASIC ACIDS.

Benzenetricarbonic Acids, $\text{C}_6\text{H}_4\text{O}_6 = \text{C}_6\text{H}_2(\text{CO}_2\text{H})_3$.

Trimesic acid (1 : 3 : 5).—Obtained by oxidation of mesitylene or uvitic acid with chromic acid mixture; also by heating mellitic acid with glycerin in an oil-bath till the mass solidifies and begins to blacken, and together with CO_2 and benzene-tetracarboxylic acid, by heating isobenzic and isohydromellitic acid with strong sulphuric acid. Short colorless prisms, rather sparingly soluble in cold water, easily in hot water, in alcohol and in ether; melts above 300°C . (572°F .), and sublimes without decomposition. By heating with excess of lime it is resolved into CO_2 and benzene. The *ethylic ether*, $\text{C}_6\text{H}_2(\text{CO}_2\text{C}_2\text{H}_5)_3$, forms long silky prisms melting at 128°C . (264.2°F .).

Hemimellitic acid (1 : 2 : 3), formed, together with phthalic anhydride, by heating hydromellic acid (p. 927) with strong sulphuric acid, crystallizes in colorless needles somewhat sparingly soluble in water. It melts at about 185°C . (365°F .), and is resolved at a higher temperature into phthalic anhydride and benzoic acid.

Trimellitic acid (1 : 2 : 4), is produced, together with isophthalic acid and pyromellitic anhydride, by heating hydropyromellitic acid with strong sulphuric acid, and abundantly, together with isophthalic acid, in the oxidation of colophony by nitric acid. It forms nodular groups of indistinct crystals, moderately soluble in water and in ether, melts at 218°C . (424.4°F .), giving off water at the same time, and being converted into the anhydride, $\text{C}_6\text{H}_2\text{O}_5 = \text{O} \begin{array}{c} \diagup \text{CO} \diagdown \end{array} \text{C}_6\text{H}_2 - \text{CO} \begin{array}{c} \diagup \text{CO} \diagdown \end{array} \text{O}$.

ol tricarbonic Acid, $C_6H_6O_7 = C_6H_2(OH)(CO_2H)_3$, is formed, with phenol-dicarbonic acid, by heating sodium salicylate in a stream of carbon dioxide, and separated as a barium salt in the manner described (p. 926). The free acid crystallizes from a hot concentrated aqueous solution in thick prisms, containing $11H_2O$; from dilute in needles with $2H_2O$. Heated above $180^\circ C.$ ($356^\circ F.$), it is, without previous fusion, into CO_2 , phenoldicarbonic acid, salicylic acid, and phenol. The *ethylic ether*, $C_6H_3(C_2H_5)_3O_7$, forms long needles, at $84^\circ C.$ ($183.2^\circ F.$).

QUADRIBASIC ACIDS.

tetracarbonic Acids, $C_6H_2(CO_2H)_4$.

There are three possible modifications of these acids, all of which have been obtained.

Pyromellitic acid (1 : 2 : 4 : 5), is obtained as anhydride, by distillation of mellitic acid, or better, by heating sodium mellitic sulphuric acid: $C_{12}H_2O_{12} = C_{10}H_2O_8 + 2CO_2 + 2H_2O$. The anhydride boiled with water yields the acid.

Mellitic acid crystallizes with $2H_2O$ in prisms slightly soluble in water, easily in hot water and in alcohol. It melts at $264^\circ C.$ ($507.2^\circ F.$), and is converted by distillation into the anhydride, $C_{10}H_2O_8$, which forms large crystals melting at $286^\circ C.$ ($546.8^\circ F.$). The salts, $C_{10}H_2Ba_2O_8$, $H_2Ca_2O_8$, are white insoluble precipitates. The *ethylic ether*, $C_{10}H_2(C_2H_5)_4$, forms short needles melting at $53^\circ C.$ ($127.4^\circ F.$).

Pyromellitic and Isohydroxypyromellitic acids, $C_{10}H_{10}O_8 = C_6H_2(CO_2H)_4$, are formed simultaneously by the action of sodium on pyromellitic acid. The former remains on evaporating its solution as a very soluble mass. The latter crystallizes with five off its water at $120^\circ C.$ ($248^\circ F.$), melts at about $200^\circ C.$ ($392^\circ F.$), and is resolved into water, CO_2 , and tetrahydrophthalic anhydride. Both acids, when heated with sulphuric acid, give off CO_2 and are converted into trimellitic and isophthalic acids.

Isopyromellitic or Prehnitic acid (1 : 2 : 3 : 5), is formed, together with CO_2 , trimesic acid and mellophanic acid, by heating hydroxypyromellitic acid with strong sulphuric acid. It crystallizes in large prisms containing $2H_2O$; dissolves easily in water, and is separated from its concentrated solution by hydrochloric acid in crystals; melts at $238^\circ C.$ ($460.4^\circ F.$), with formation of anhydride.

Prehnitic acid, prepared like hydroxypyromellitic acid, is a gummy solid, which is dissolved by heating with strong sulphuric acid into CO_2 , prehnitic acid, and isophthalic acid.

Mellophanic acid, produced, together with prehnitic acid, forms distinct anhydrous crystals united in crusts; melts at $215^\circ - 238^\circ C.$ ($400.4^\circ F.$). With sodium-amalgam it yields hydromellophanic acid.

HEXATOMIC ACID.

Mellitic Acid, $C_{12}H_2O_{12} = C_6(CO_2H)_6$.—This acid, having the constitution of benzene in which all the six hydrogen-atoms are replaced by carboxyl groups, occurs as aluminium salt in *mellite* or *honey-stone*, a mineral found in

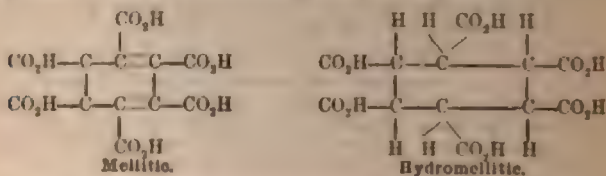
beds of lignite. It is soluble in water and alcohol, and crystallizes in colorless needles, melts when heated, and is resolved by distillation into CO_2 , water, and pyromellitic anhydride; by heating with lime, into CO_2 and benzene. It is a very stable acid, not being decomposed by sulphuric, nitric, or hydriodic acid, or by bromine; even with the aid of heat. Mellitic acid forms acid and neutral salts and ethers, whose composition may be illustrated by the following examples:

| Neutral. | Acid. |
|--|--|
| $\text{C}_{10}(\text{NH}_4)_6\text{O}_{12}$ | $\text{C}_{12}\text{H}_4(\text{NH}_4)_3\text{O}_{12}$ |
| $\text{C}_{12}(\text{CH}_3)_6\text{O}_{12}$ | $\text{C}_{12}\text{H}_2\text{K}_2\text{O}_{12}$ |
| $\text{C}_{12}(\text{C}_2\text{H}_5)_6\text{O}_{12}$ | $\text{C}_{12}\text{H}_2(\text{C}_2\text{H}_5)_3\text{O}_{12}$ |
| $\text{C}_{12}\text{Ba}_3\text{O}_{12}$ | $\text{C}_{12}\text{H}_2\text{Cu}_3\text{O}_{12}$ |
| $\text{C}_{12}(\text{Al}_2)_3\text{O}_{12}$ | |

Ammonium mellitate yields by distillation *paramide* and *euchroic acid*. The former is a white amorphous substance, containing $\text{C}_{12}\text{H}_4\text{N}_2\text{O}_6$ (i. e., tri-ammonic mellitate, $\text{C}_{12}\text{H}_4(\text{NH}_4)_3\text{O}_{12} - 6\text{H}_2\text{O}$), and convertible by boiling with water into acid ammonium mellitate. *Euchroic acid*, $\text{C}_{12}\text{H}_4\text{N}_2\text{O}_8$ [$= \text{C}_{12}\text{H}_4(\text{NH}_4)_2\text{O}_{12} - 4\text{H}_2\text{O}$], forms colorless, sparingly soluble crystals. In contact with zinc and deoxidizing agents in general, it yields a deep blue insoluble substance called *euchrone*.

Hydromellitic acid, $\text{C}_{12}\text{H}_{12}\text{O}_{12} = \text{C}_6\text{H}_6(\text{CO}_2\text{H})_6$, is slowly formed by the action of sodium-amalgam on ammonium mellitate. Colorless indistinct crystals, easily soluble in water. Sexbasic. Changes slowly by keeping, quickly, when heated to 180°C . (356°F .) with strong hydrochloric acid, into isohydromellitic acid, $\text{C}_{12}\text{H}_{12}\text{O}_{12}$, which crystallizes in thick, hard four-sided prisms, dissolves readily in water, and is precipitated from the solution by hydrochloric acid. Both these acids, heated with strong sulphuric acid, yield a mixture of prehnitic, mellophanic, and trimelic acids.

Hydromellitic acid is an additive compound, in which the double linking of the alternate pairs of carbon-atoms in the benzene nucleus is broken up by the entrance of the additional hydrogen-atoms:

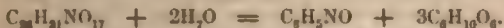


INDIGO GROUP.

Indigo-blue and its immediate derivatives form a group of bodies nearly related to the benzene-group, as shown by their products of decomposition (aniline, ortho-amidobenzoic acid, etc.); but their constitution cannot yet be regarded as precisely determined, for want of sufficiently definite modes of synthetic formation.

Indigo-blue or **Indigotin**, $\text{C}_8\text{H}_5\text{NO}$ or $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$, probably
 $\text{N}-\text{C}_6\text{H}_4-\text{CO}-\text{CH}$
 $\parallel \quad \parallel$
 $\text{N}-\text{C}_6\text{H}_4-\text{CO}-\text{CH}$.—Indigo is the product of several species of plants of

the genus *Indigofera*, growing in India and South America, also of *Isatis factoria*, *Nerium tinctorium*, *Polygonum tinctorum*, and other plants. It does not exist in these plants ready-formed, but is produced by decomposition of a glucoside, $C_{25}H_{31}NO_{17}$, called *indican*, which may be extracted from them by cold alcohol, and forms a brown bitter syrup, easily soluble in water and alcohol. This substance, when boiled with dilute acids, or subjected to the action of ferments, is resolved into indigo-blue and indigluoin, $C_{16}H_{16}O_4$:



A substance similar to indican sometimes occurs in urine, and gives rise, by its conversion into indigo-blue, to a blue coloration of the liquid when left in contact with the air, or treated with sulphuric acid.

To obtain indigo from the plants which produce it, the chopped leaves and twigs are macerated in water for 12 to 15 hours, after which the liquid is poured off into shallow wooden vessels, and frequently stirred, so as to bring it as much as possible into contact with the air. The indigo thereby deposited is separated from the brown liquid, boiled with water, and dried.

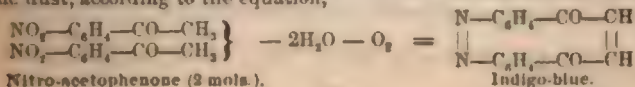
Commercial indigo is a mixture of several substances, all of which, except indigo-blue, are useless to the dyer. Boiling with dilute acetic acid extracts *indigo-gelatin*; dilute potash-lye then extracts *indigo-brown*; and the residue yields to boiling alcohol *indigo-red*, which remains on evaporation as a red powder, soluble in alcohol and ether. The residue left after boiling with alcohol is nearly pure indigo-blue.

Pure indigo-blue may be obtained from the commercial product by cautious sublimation; it then rises as a fine purple vapor, which condenses in dark-blue needles having a coppery lustre.

The best method of effecting the sublimation, is to mix 1 part of powdered indigo with 2 parts of plaster-of-Paris, make the whole into a paste with water, and spread it upon an iron plate. This, when quite dry, is heated by a spirit-lamp; the volatilization of the indigo is aided by the vapor of water disengaged from the gypsum; and the surface of the mass becomes covered with beautiful crystals of pure indigo, which may be easily removed by a thin spatula. At a higher temperature, charring and decomposition take place.

The best method of obtaining indigo-blue is to reduce the crude product to indigo-white by the action of ferrous sulphate or glucose in alkaline solution, and then reoxidize it. It is on this principle that the dyer prepares his *indigo-cat*: 5 parts of powdered indigo, 10 parts of green vitriol, 15 parts of slaked lime, and 60 parts of water, are agitated together in a close vessel, and then left to stand. The ferrous hydrate, in conjunction with the excess of lime, reduces the indigo to the soluble state; and a yellowish liquid is produced, from which acids precipitate indigo-white, as a flocculent substance which absorbs oxygen with the greatest avidity, and becomes blue. Cloth, steeped in the alkaline liquid, and then exposed to the air, acquires a deep and permanent blue tint by the deposition of solid insoluble indigo in the substance of the fibre.—Instead of the iron salt and lime, a mixture of dilute caustic soda and grape-sugar dissolved in alcohol may be used; the sugar becomes oxidized to formic acid, and the indigo reduced. On allowing such a solution to remain in contact with the air, it absorbs oxygen, and deposits indigo-blue in the crystalline state.

Indigo-blue is said to have been obtained by treating liquid nitro-acetophenone (p. 892) dissolved in chloroform with a mixture of soda-lime, and fine dust, according to the equation,



But the quantity of indigo-blue thus obtained is always very small, and it appears to be very difficult to ascertain the precise conditions under which the transformation takes place.*

Indigo-white or Hydrindigotin, $C_{16}H_{12}N_2O_2$, is precipitated by hydrochloric acid from its alkaline solution (formed as above), out of contact with the air, as a white crystalline powder, dissolving with yellow color in alcohol, ether, and alkalis. It is converted into indigo-blue by exposure to the air, and into indol by distillation with zinc-dust.

Indigo-Sulphonic Acids.—When indigo-blue is heated for a considerable time with 5 to 15 parts of strong sulphuric acid, it dissolves, with formation of a mono- and di-sulphonic acid.

Indigo-monosulphonic acid, $C_{16}H_9N_2O_2 \cdot SO_3H$ (*Sulphoindigotin* or *Phenylsulphonic acid*), separates, on diluting the solution with water, as a blue powder, soluble in pure water and in alcohol, but insoluble in dilute acids. Its salts are red in the solid state, but dissolve in water with blue color.

Indigo-disulphonic acid, $C_{16}H_8N_2O_2(SO_3H)_2$ (*Sulphindigotin* or *Sulphindigic acid*), remains in the filtrate from the monosulphonic acid, and constitutes the sole product when 15 parts of sulphuric acid are used to dissolve 1 part of indigo. To separate the acid, clean white wool, previously boiled with solution of sodium carbonate, is dipped into the liquid, and as soon as it has acquired a dark blue color, it is taken out, washed with water, and boiled with ammonium carbonate; the resulting solution is precipitated with lead acetate, and the precipitate decomposed by hydrogen sulphide. In this manner a colorless solution of hydrindigotin-disulphonic acid, $C_{16}H_{12}N_2O_2(SO_3H)_2$, is obtained, which, on exposure to the air, is quickly converted by oxidation into the disulphonic acid of indigo-blue, which, on evaporating the solution, remains in the form of a blue amorphous mass. The salts, $C_{16}H_8N_2O_2(SO_3K)_2$ and $C_{16}H_8N_2O_2(SO_3Na)_2$, known in commerce as indigo-carmin, are prepared on the large scale by adding potassium acetate or sodium sulphate to a dilute solution of indigo-blue in sulphuric acid, washing the blue precipitate with solutions of the same salts, and pressing it. They form copper-colored masses, blue in the finely-divided state, and dissolving with blue color in pure water.

Isatin, $C_8H_5NO_2 = C_8H_4 \begin{matrix} \diagup CO-C(OH) \\ \diagdown N \end{matrix}$, is obtained by oxidizing in-

digo with chromic, or better, with nitric acid. Powdered indigo is mixed with water to a thin paste, heated to the boiling point in a large capsule, and nitric acid is added by small portions until the blue color disappears; the whole is then largely diluted with boiling water, and filtered. The impure isatin which separates on cooling is washed with water containing a little ammonia, and recrystallized. The process requires careful management, or the oxidizing action proceeds too far, and the product is destroyed.

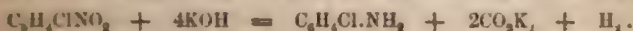
Isatin forms deep yellowish-red prismatic crystals, sparingly soluble in cold water, freely in boiling water and in alcohol. The solution colors the skin yellow, and causes it to emit a very disagreeable odor. Isatin when heated melts and sublimes, with partial decomposition. It unites with acid sulphites of alkali-metal, forming crystalline compounds. It dissolves in

* Emmerling and Engler, Deutsch. Chem. Ges. Ber. ix. 1422; Chem. Soc. Journal, 1877, i. 321.

alkalies, forming violet solutions, from which silver nitrate throws down a red precipitate of $C_8H_7AgNO_2$. On boiling these solutions, the isatin is converted into isatic acid, and the color changes to yellow.

Isatin is converted by nitrous acid into nitrosalicylic acid. Distilled with strong potash-solution it yields aniline. On heating it to $80^\circ C.$ ($176^\circ F.$), with phosphorus trichloride and phosphorus, dissolving the product in water, and leaving the solution exposed to the air for twenty-four hours, it deposits indigo-blue.

Chlorinated and Brominated derivatives of Isatin (mono- and di-), e. g., $C_8H_5ClNO_2$, $C_8H_3Cl_2NO_2$, etc., are formed by passing chlorine or bromine into the hot aqueous solution of isatin. These compounds crystallize well, and are converted by fusion with potash into substituted anilines; e. g.,



Isatin boiled with ammonia yields amido-derivatives, which have been but little examined. By reducing agents it is converted into isatyde, $C_{16}H_{17}N_2O_4$.

Isatinsulphonic acid, $C_8H_5NO_2.SO_3H$, formed by oxidation of indigosulphonates (indigo-carmin), is very soluble, and crystallizes with difficulty: it forms derivatives analogous to those of isatin.

Isatyde or Hydroisatin, $C_8H_6NO_2$, is formed when isatin is warmed with dilute sulphuric acid, or when its warm, saturated, alcoholic solution is mixed in a closed flask with ammonium hydrosulphide, the liquid then gradually depositing the isatyde in colorless crystalline scales. It is tasteless, insoluble in water, slightly soluble in alcohol.

Thioisatyde, $C_{16}H_{17}N_2S_2O_2$, is formed on passing hydrogen sulphide into an alcoholic solution of isatin, and is precipitated on dropping the filtered solution into water. It is a grayish-yellow, pulverulent, uncrystallizable substance, which softens in hot water, and dissolves in alcohol.

Indin, $C_{16}H_{16}N_2O_2$ (isomeric or polymeric with indigo-blue), is formed on triturating thioisatyde with potassium hydroxide, gradually adding alcohol, and washing the reddened mass with water; also by boiling a solution of dioxindol in glycerin. It is a crystalline powder of a fine rose-color, insoluble in water, slightly soluble in alcohol. It dissolves when heated with alcoholic potash, and the solution, on cooling, deposits potassium-indin, $C_{16}H_8KN_2O_2$, in small black crystals.

Isatic Acid, or **Trioxindol**, $C_8H_7NO_3$.—The violet solution of isatin in potash-lye turns yellow when heated, and then contains *potassium isatate*, $C_8H_6KNO_3$, which is deposited on evaporation in yellow crystals. This salt, decomposed with an acid, yields isatic acid as a white powder, soluble in water, and resolved by heat into isatin and water.

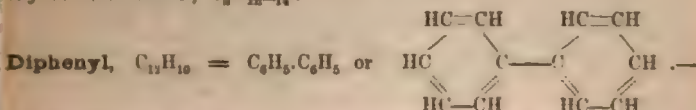
Hydrindic Acid, or **Dioxindol**, $C_8H_7NO_2$, is formed by the action of sodium on isatin suspended in water, or dissolved in an alkali, isatic acid being first formed, and then reduced. It crystallizes in yellow prisms, is soluble in water and in alcohol, and forms crystalline compounds both with bases and with acids. It melts at $180^\circ C.$ ($356^\circ F.$), and decomposes at $195^\circ C.$ ($383^\circ F.$), with formation of aniline. The aqueous solution turns red on exposure to the air, from formation of isatin: when boiled with ammonia it turns violet. Metallic salts added to the solution throw down crystalline compounds, such as $C_8H_5AgNO_3$ and $C_8H_5PbNO_3 + H_2O$.

Dioxindol treated with nitrous acid in alcoholic solution is converted

DIPHENYL GROUP.

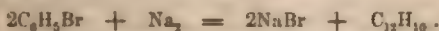
The compounds of this group contain two or more benzene-nuclei, united either directly or through the medium of other carbon groups.

Hydrocarbons, $C_{12}H_{10-14}$:



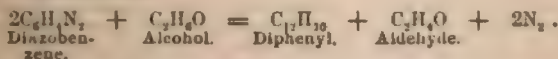
This hydrocarbon is formed: (1) By passing benzene-vapor through a red-hot tube containing fragments of pumice: $2C_6H_6 = C_{12}H_{10} + H_2$. This is the best method of preparing it, the yield amounting to about 30 per cent. of the benzene used.

(2) By the action of sodium on bromobenzene (phenyl bromide) dissolved in ether or benzene:



(3) By heating a mixture of potassium phenate and benzoate or oxalate, and small quantity (together with benzene) by heating benzoic acid 4th time.

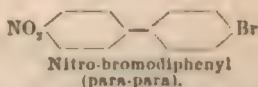
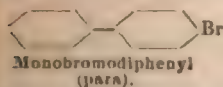
(4) Together with other products, by the action of alcoholic potash onurate of diazobenzene:



Diphenyl appears also to be one of the constituents of crude anthracene (p. 951), and passes over in the distillation of that substance at about $200^\circ C.$ ($500^\circ F.$).

Diphenyl crystallizes from alcohol in iridescent nacreous scales, melts at about $70.5^\circ C.$ ($158.9^\circ F.$), sublimes at a higher temperature, and boils at $240^\circ C.$ ($489.2^\circ F.$). When dissolved in glacial acetic acid it is oxidized by chromic anhydride to benzoic acid.

Diphenyl, subjected to the action of halogens, nitric acid, and sulphuric acid, yields mono- and di-substitution-derivatives. In the former, such as $C_{12}H_9Br$, $C_{12}H_9(NO_2)$, $C_{12}H_9(SO_3H)$, the substituted radicles stand in the place of junction of the two benzene-nuclei in the para-position. The di-derivatives are known in two isomeric modifications, the most frequent being those in which both the substituted groups are in the para-position relatively to the point of junction:



By oxidation with chromic anhydride, the monosubstituted diphenyls and para-derivatives of benzoic acid, the group C_6H_4Br , for example, being oxidized to (1 : 4) bromobenzoic acid, while the other group (C_6H_5) is broken up. The di-derivatives, on the other hand, are converted by oxidation into two para-derivatives of benzoic acid, e. g., $C_6H_4(NO_2).C_6H_4Br$ into *p*-nitro- and *p*-bromobenzoic acid.

Monochlorodiphenyl, $C_{12}H_9Cl$, formed by the action of PCl_5 on oxyphenyl ($C_{12}H_9OH$), forms colorless crystals melting at $75^\circ C.$ (167°

F.). *Dichlorodiphenyl*, $C_{12}H_9Cl_2$, from benzidine, melts at $148^\circ C.$ ($298.4^\circ F.$).

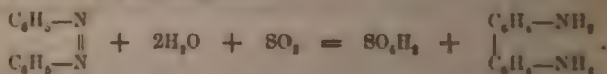
Bromodiphenyl, $C_{12}H_9Br$, forms laminae, melts at $89^\circ C.$ ($192.2^\circ F.$), boils at $310^\circ C.$ ($590^\circ F.$). $C_{12}H_9Br_2$ forms prisms melting at $164^\circ C.$ ($327.2^\circ F.$).

Cyanodiphenyl, $C_{12}H_9CN$, obtained by dry distillation of a mixture of diphenyl-monosulphonate and cyanide of potassium, forms hard colorless crystals, melting at 84° – $85^\circ C.$ (183.2° – $185^\circ F.$), insoluble in water, easily soluble in alcohol. *Di-cyanodiphenyl*, $C_{12}H_6(CN)_2$, obtained in like manner from diphenyldisulphonic acid, forms ramified colorless needles melting at $234^\circ C.$ ($453.2^\circ F.$), sparingly soluble in cold, freely in boiling alcohol.

Nitrodiphenyl, $C_{12}H_9(NO_2)$, crystallizes in needles, melts at $113^\circ C.$ ($233.6^\circ F.$), boils at $340^\circ C.$ ($644^\circ F.$). An isomeric compound obtained by distilling calcium meta-nitrobenzoate with potassium phenate, melts at $86^\circ C.$ ($186.8^\circ F.$), according to Pfankuch, at $157^\circ C.$ ($314.6^\circ F.$), according to Schultz.* Two *dinitro-compounds*, $C_{12}H_6(NO_2)_2$, are formed by the action of fuming nitric acid on diphenyl; the less soluble in alcohol of the two melts at $213^\circ C.$ ($415.4^\circ F.$), and boils $340^\circ C.$ ($644^\circ F.$), the more soluble compound melts at $93.5^\circ C.$ ($200.3^\circ F.$).

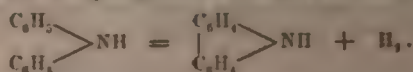
Amidodiphenyls are formed by the reduction of the nitro-compounds with tin and hydrochloric acid. — *Xenylamine*, $C_{12}H_9(NH_2)$, crystallizes from hot water or alcohol in colorless laminae melting at $49^\circ C.$ ($120.2^\circ F.$).

Benzidine, $C_{12}H_8(NH_2)_2$, is also produced by the action of sodium on monobromaniline, and by molecular transposition of hydrazobenzene in contact with acids (p. 852); further, by heating azobenzene with fuming hydrochloric acid to $115^\circ C.$ ($239^\circ F.$), and by passing SO_2 into the alcoholic solution of that compound:



Benzidine crystallizes in silvery laminae, easily soluble in hot water and alcohol, melting at $118^\circ C.$ ($244.4^\circ F.$), and subliming with partial decomposition. It is a bivalent base. The *sulphate*, $C_{12}H_{10}N_2 \cdot SO_4H_2$, is nearly insoluble in water and alcohol.

Diphenylimide or Carbazol, $C_{12}H_9N$, is formed by passing the vapor of aniline or of diphenylamine through a red-hot tube:



It occurs in coal-tar oil (320° – $360^\circ C.$, 608° – $680^\circ F.$), and as a by-product in the manufacture of aniline.

Carbazol crystallizes in shining laminae, soluble in hot alcohol, ether, and benzene; melts at $238^\circ C.$ ($460.4^\circ F.$), and distills at 354° – $356^\circ C.$ (669.2° – $671^\circ F.$). It dissolves in strong sulphuric acid, with yellow color, readily changed to green by oxidizing agents. With picric acid, it forms a compound which crystallizes in red needles melting at $182^\circ C.$ ($359.6^\circ F.$).

Acridine, $C_{17}H_9N$, isomeric with carbazol, likewise occurs in coal-tar oil, and may be extracted by sulphuric acid from the portion boiling be-

* Liebig's Annalen, clxxiv. 201; Jahresbericht für Chemie, 1874, 606.

tween 320°C . (608°F .) and 360°C . (680°F .). It forms rhombic crystals, easily soluble in alcohol and ether, melts at 107°C . (224.6°F .), sublimes in broad needles at 100°C , boils at a temperature above 360°C . (680°F .). It unites with acids (carbazol does not) forming salts which are decomposed by boiling with a large quantity of water.

Diphenylsulphonic acids, $\text{C}_{12}\text{H}_{10}(\text{SO}_3\text{H})$ and $\text{C}_{12}\text{H}_8(\text{SO}_3\text{H})_2$, are formed by heating diphenyl with strong sulphuric acid, the former, however, only when a very small quantity of sulphuric acid is used. The disulpho-acid crystallizes in long deliquescent prisms, melting at 72.5°C . (161.6°F .). These acids fused with potash yield the corresponding phenols, $\text{C}_{12}\text{H}_9(\text{OH})$ and $\text{C}_{12}\text{H}_7(\text{OH})_2$.

Hydrocarbons, $\text{C}_{12}\text{H}_{12}$:—

Phenyl-tolyl, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$, is formed by the action of sodium on a mixture of bromobenzene and parabromotoluene diluted with ether. It is a colorless liquid of specific gravity 1.015 at 27° (80.6°F .), boiling at $263\text{--}267^{\circ}\text{C}$. ($505.4\text{--}512.6^{\circ}\text{F}$.), solidifying in a freezing mixture.

Diphenylmethane, $\text{C}_{12}\text{H}_{12} = \text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ (*Benzyl-benzene*), is obtained by heating a mixture of benzene (6 parts) and benzyl chloride (10 parts) with zinc-dust (3 or 4 parts) in a vessel with reversed condenser. Colorless crystalline mass made up of needles, and having an odor of oranges; melts at $26\text{--}27^{\circ}\text{C}$. ($78.8\text{--}80.6^{\circ}\text{F}$.), boils at $261\text{--}262^{\circ}\text{C}$. ($501.8\text{--}503.6^{\circ}\text{F}$.); dissolves easily in alcohol and ether. Passed through a red-hot tube it yields diphenylene-methane, $\text{C}_{12}\text{H}_{10}$. Chromic acid mixture oxidizes it to diphenyl ketone, $\text{CO}(\text{C}_6\text{H}_5)_2$. It dissolves in strong nitric acid, forming two dinitro-derivatives.

Diphenyl-chloromethane, $\text{C}_6\text{H}_5\text{—CHCl—C}_6\text{H}_5$, formed by the action of HCl on benzhydrol (p. 940), is a crystalline mass melting at 14°C . (57.2°F .).

Hydrocarbons, $\text{C}_{14}\text{H}_{14}$:—

Bitolyl, $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{CH}_3 \\ | \\ \text{C}_6\text{H}_4\cdot\text{CH}_3 \end{array}$, produced by the action of sodium on parabromotoluene, forms monoclinic crystals, easily soluble in hot alcohol, melting at 121°C . (249.8°F .).

Dibenzyl, $= \text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$, formed by the action of sodium on benzyl chloride, and by heating stilbene, toluene, benzoin, deoxybenzoin, or toluylene hydrate, with hydriodic acid, crystallizes in large colorless prisms, melts at 52°C . (125.6°F .), boils at 284°C . (543.2°F .); dissolves easily in hot alcohol. Heated to 500°C . (932°F .) it yields stilbene and toluene: $2\text{C}_{14}\text{H}_{14} = \text{C}_{14}\text{H}_{12} + 2\text{C}_7\text{H}_8$.

Diphenyl-ethane, $\text{C}_{14}\text{H}_{12} = (\text{C}_6\text{H}_5)_2\text{CH—CH}_3$, is formed by the action of sulphuric acid on a mixture of paraldehyde and benzene ($2\text{C}_6\text{H}_6 + \text{C}_3\text{H}_4\text{O} = \text{H}_2\text{O} + \text{C}_{14}\text{H}_{12}$). Colorless liquid, boiling at $268\text{--}270^{\circ}\text{C}$. ($514.4\text{--}518^{\circ}\text{F}$.), solidifying in a freezing mixture: oxidized by chromic acid mixture to benzophenone.

A mixture of 2 mol. benzene and 1 mol. chloral or bromal with strong sulphuric acid, yields in like manner, diphenyltrichlorethane, $(\text{C}_6\text{H}_5)_2\text{CH—CCl}_3$ (colorless laminae melting at 64°C . 147.2°F .), or diphenyltribromethane, $(\text{C}_6\text{H}_5)_2\text{CH—CBr}_3$ (monoclinic crystals, m. p. 89°C . 192.2°F .). A mixture of benzene and dichlorethylic oxide, $(\text{C}_2\text{H}_3\text{Cl})_2\text{O}$, similarly treated, yields *diphenyl-monochlorethane*, $(\text{C}_6\text{H}_5)_2\text{CH—CH}_2\text{Cl}$, as an oil which decomposes when distilled.

Benzyl-toluene, $C_{11}H_{14} = C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot CH_3$, formed by passing the vapors of paraphenyl-tolyl ketone, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot CH_3$, over heated zinc-dust, is a colorless liquid boiling at 255°C . (540°F .), not solidifying at -20°C . (-4°F .).

Hydrocarbons, $C_{12}H_{16}$:—

Titolyl-methane, $C_6H_5 \cdot \begin{smallmatrix} CH_3 \\ | \\ CH_2 \end{smallmatrix} \cdot C_6H_5 \cdot CH_3$, formed by the action of sulphuric acid on a mixture of methylal, $CH_2(OCH_3)_2$ (p. 500), toluene, and glacial acetic acid, is a liquid not solidifying at -15°C . (5°F .), boiling at 290°C . (554°F .). $C_{12}H_{14}Br_2$, forms long needles melting at 115°C . (239°F .). $C_{12}H_{14}(NO_2)_2$, forms colorless crystals melting at 164°C . (327.2°F .).

Dibenzyl methane, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, from dibenzyl ketone by heating with HI and phosphorus, is a non-solidifiable liquid, boiling at 294°C . (561.2°F .).

Benzyl-ethyl-benzene, $C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot C_2H_5$, from benzyl chloride and benzene, is a colorless liquid boiling at 294°C . (561.2°F .).

Ethyl-benzene-toluene or Phenyltolyl-ethane,

$CH_3 \cdot CH \cdot \begin{smallmatrix} C_6H_5 \cdot CH_3 \\ | \\ C_6H_5 \end{smallmatrix}$, formed by heating bromethyl-benzene (p. 827) and toluene with zinc-dust, is a liquid boiling at 278°C . (532.4°F .).

Hydrocarbons, $C_{16}H_{18}$:—

Titolyethane, $CH_3 \cdot CH(C_6H_4 \cdot CH_3)_2$, obtained, like diphenyl-ethane, from paraldehyde, toluene, and sulphuric acid, is a liquid, boiling at 298°C . (568.4°F .), not solidifying at -20°C . (-4°F .).

Similarly, by the use of chloral instead of paraldehyde, is obtained $CHCl \cdot CH(C_6H_4 \cdot CH_3)_2$, in crystals melting at 89°C . (192.2°F .), and with dichlorethylidene oxide, $CH_2Cl \cdot CH(C_6H_4 \cdot CH_3)_2$.

Diphenyldimethylethane, $C_6H_5 \cdot CH \cdot CH_2 \cdot \begin{smallmatrix} | \\ C_6H_5 \cdot CH \cdot CH_2 \end{smallmatrix}$, obtained by the action of

sodium on secondary phenyl-ethyl chloride, $C_6H_5 \cdot CHCl \cdot CH_2$ (p. 852), forms needles melting at 123.5°C . (254.3°F .).

Diphenylene-methane or Fluorene, $C_{15}H_{12} = \begin{smallmatrix} C_6H_5 \\ | \\ C_6H_4 \\ | \\ C_6H_5 \end{smallmatrix} > CH_2$, is formed

by heating diphenylene ketone with zinc-dust or with hydroflic acid and amorphous phosphorus to 160°C . (320°F .), also by passing the vapor of diphenylene-methane through a red-hot tube. It is contained in the portion of coal-tar oil boiling at 300°C . (572°F .). It crystallizes from hot alcohol in colorless laminae, exhibiting a beautiful violet fluorescence; melts at 112°C . (233.6°F .), boils at 305°C . (581°F .); unites with picric acid, forming a compound which crystallizes in red needles melting at 80°C . (176°F .). By oxidation with chromic acid mixture it yields diphenylene-ketone, $CO(C_6H_4)_2$.

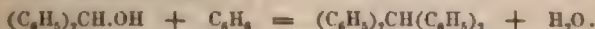
Diphenyl-benzene, $C_{18}H_{14} = C_6H_5 \cdot (C_6H_4)_2$, is formed by the action of sodium on a mixture of bromobenzene and paralibromobenzene, and, together with an isomeric compound, by passing a mixture of diphenyl and

benzene through red-hot tubes: hence these two isomeric compounds are obtained, as secondary products, in the preparation of diphenyl.—Diphenylbenzene forms groups of needles slightly soluble in hot alcohol and ether, melting at 205°C . (401°F .), subliming easily and boiling at 400°C . (752°F .). By chromic anhydride and glacial acetic acid it is oxidized to diphenylcarbonic, and afterwards to terephthalic acid.—*Isodiphenyl benzene* melts at 85°C . (185°F .), and boils at about 360°C . (680°F .).

Triphenyl-methane, $\text{C}_{19}\text{H}_{15} = \text{C}_6\text{H}_5\text{—CH}(\text{C}_6\text{H}_5)_2$, is formed by heating benzal chloride to 150°C . (302°F .) with mercury-diphenyl:



also by heating benzhydrol (p. 940) with benzene and phosphoric anhydride to 140°C . (284°F .).



Shining laminae, melting at 92°C . (197.6°F .), boiling at about 360°C . (680°F .). By bromine and water it is converted into triphenyl carbinol, which melts at 157°C . (314.6°F .).

Tolyl-diphenyl-methane, $\text{C}_{20}\text{H}_{18} = (\text{C}_6\text{H}_5)_2\text{CH—C}_6\text{H}_4\text{—CH}_3$, prepared, like the preceding, from benzhydrol and toluene, is a colorless liquid of high boiling point.

Triphenyl-benzene, $\text{C}_{24}\text{H}_{18} = \text{C}_6\text{H}_5(\text{C}_6\text{H}_5)_3$, obtained by heating acetophenone (p. 892) with phosphoric anhydride, forms large rhombic crystals, melts at 169°C . (336.2°F .), boils above 360°C . (680°F .), dissolves easily in alcohol and in benzene.

Tetraphenyl-ethane, $\text{C}_{26}\text{H}_{22} = (\text{C}_6\text{H}_5)_2\text{CH—CH}(\text{C}_6\text{H}_5)_2$, obtained by the action of zinc on a solution of benzhydrol, $\text{C}_6\text{H}_5\text{.CHOH.C}_6\text{H}_5$, mixed with fuming hydrochloric acid, forms large prisms melting at 209°C . (408.2°F .).

Ethene-derivatives.

Diphenyl-ethene, $\text{C}_{14}\text{H}_{12}$.—Of this hydrocarbon there are two modifications, symmetrical and unsymmetrical.

1. *Stilbene* or *Toluylene*, $\text{C}_6\text{H}_5\text{—CH=CH—C}_6\text{H}_5$, is formed in a variety of reactions, especially by dry distillation of benzyl sulphide or disulphide (p. 882); by the action of sodium on benzaldehyde or benzal chloride; and by passing the vapor of dibenzyl or of toluene over heated lead oxide. It is most easily obtained from benzyl sulphide.

Stilbene crystallizes in large laminae, dissolves easily in hot alcohol, melts at 125°C . (257°F .), distils at $306^{\circ}\text{—}307^{\circ}\text{C}$. ($582.8^{\circ}\text{—}584.6^{\circ}\text{F}$.). By heating with hydriodic acid it is converted into dibenzyl; by oxidation with chromic acid mixture into benzaldehyde and benzoic acid. It unites with bromine, forming $\text{C}_{14}\text{H}_{12}\text{Br}_2$ (crystals, melting at 230°C ., 446°F .), which is also produced by the action of bromine, without cooling, on dibenzyl. By alcoholic potash this bromide is converted into bromostilbene, $\text{C}_{13}\text{H}_{11}\text{Br}$ (crystals, m. p. 25°C ., 77°F .), and toluene.

2. *Isostilbene*, $\text{CH}_2\text{—C}(\text{C}_6\text{H}_5)_2$, *unsymmetric diphenylethene*, obtained by boiling diphenyl-monochlorethane (p. 935) with alcoholic potash, is a

colorless non-solidifying oil, which boils at 277°C . (530.6°F .), and is converted by oxidation into diphenyl-ketone.

Tetraphenyl-ethene, $\text{C}_{26}\text{H}_{20} = (\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$, obtained by the action of finely divided silver on benzophenone chloride, and, together with diphenyl-methane, and other hydrocarbons, by heating benzophenone with zinc-dust, is a white crystalline powder, melting at 221°C . (429.8°F .), sparingly soluble in alcohol and ether, easily in benzene.

Tolane, $\text{C}_{11}\text{H}_{10} = \text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$, *Diphenyl acetylene*, obtained by boiling stilbene bromide with alcoholic potash, forms large crystals, melting at 60°C . (140°F .), easily soluble in alcohol and ether. It forms two dibromides, $\text{C}_{11}\text{H}_8\text{Br}_2$, (m. p. 64°C ., 147.2°F ., and 200°C .– 205°C ., 392 – 404°F .), easily convertible one into the other; and two dichlorides (m. p. 63° and 153°C ., 145.4° – 307.4°F .).

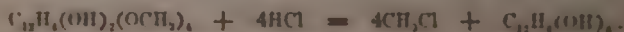
Phenols.

Oxydiphenyl or Diphenylol, $\text{C}_{12}\text{H}_8\text{O} = \text{C}_6\text{H}_5-\text{C}_6\text{H}_4\text{OH}$, is formed by fusing the potassium salt of diphenylsulphonic acid, $\text{C}_{12}\text{H}_7\text{SO}_3\text{K}$, with potassium hydroxide, and by the action of potassium nitrite on anisole-phenyl sulphate. Colorless monoclinic crystals, melts at 164 – 165°C . (327.2° – 329°F .), boils at 305° – 308°C . (581° – 586.4°F .); volatilizes with vapor of water; dissolves easily in alcohol, ether, and alkalies; and with fine green color in strong sulphuric acid.

Dioxydiphenyl or Diphenol, $\text{C}_{12}\text{H}_8(\text{OH})_2 = \text{C}_6\text{H}_4(\text{OH})_2$, is formed by the action of melting potash on potassium diphenyl-*para*-sulphonate; also from benzidine by the diazo-reaction; and by fusing potassium *para*-phenol-sulphonate with alkalis. Colorless rhombic crystals, melting at 156° – 158°C . (312.8° – 316.4°F .). An isomeric compound, which crystallizes from alcohol in shining needles melting at 268° – 270°C . (516.2° – 518°F .), is formed by the action of melting potash on potassium diphenyl-disulphonate.

Diphenylene Oxide, $\text{C}_{12}\text{H}_8\text{O} = \begin{matrix} \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_4 \\ | \end{matrix} \text{O}$, formed by heating phenyl phosphate with lime, or more readily by heating phenol with lead oxide, crystallizes in laminae, melts at 81°C . (177.8°F .), and boils at 272 – 273°C . (523.4°F .).

Hexoxydiphenyl, $\text{C}_{17}\text{H}_{10}\text{O}_6 = \text{C}_{12}\text{H}_8(\text{OH})_6$, is formed from its tetramethylene ether (hydrocærulignone) by the action of strong hydrochloric or hydriodic acid:



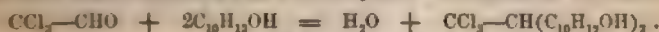
It crystallizes from water in silvery laminae; dissolves in potash-lye with fine blue-violet color; is converted by acetyl chloride into a hexaacetyl compound; and reduced by heating with zinc-dust to diphenyl.

Hydrocærulignone, $\text{C}_{12}\text{H}_8 \begin{Bmatrix} (\text{OCH}_2)_4 \\ (\text{OH})_6 \end{Bmatrix}$, is formed from cornuignone by the action of tin and hydrochloric acid. It crystallizes from alcohol in

colorless laminae, melts at 190° C. (374° F.) and distills almost without decomposition. It is a diatomic phenol, and is resolved by HCl or HI into CH₃Cl and hexoxydiphenyl.

Cærulignone, C₁₆H₁₄O₄ = C₁₂H₄ { (OCH₃)₄ }₄, separates as a violet powder in the industrial purification of crude wood-vinegar by means of potassium dichromate, and is obtained by the same means from the fraction of beech-tar boiling at 270° C. (518° F.). It is insoluble in most solvents, but dissolves in strong sulphuric acid with a fine corn-flower blue color, changing for a while to red on addition of a large quantity of water; also in phenol, from which it is precipitated by alcohol and ether in slender steel-blue needles. By reduction with tin and hydrochloric acid, it is converted into colorless hydrocærulignone, C₁₆H₁₈O₄, which is reconverted into cærulignone by oxidation, the two bodies being indeed related to one another in the same manner as quinone and hydroquinone.

Dithymoxyl-trichlorethane,* CCl₃—CH(C₁₀H₁₂OH)₂, is formed when sulphuric acid diluted with $\frac{1}{2}$ vol. of glacial acetic acid is added to a cooled mixture of 1 mol. chloral and 2 mol. thymol:



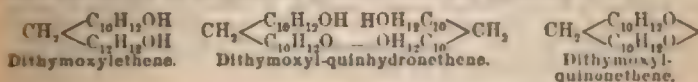
A white precipitate is then formed, the alcoholic solution of which yields the compound in white monoclinic crystals.

Dithymoxyl-trichlorethane is a diatomic phenol, and when treated with C₂H₅OCl or C₇H₅OCl, exchanges its two phenolic hydrogens for acetyl or benzoyl. By strong oxidizing agents it is converted into thymoquinone. Heated with zinc-dust, it exchanges its chlorine for hydrogen, forming dithymoxylethane, C₂₂H₂₆O₂, part of which is converted by loss of H₂ into dithymoxylethene, C₂₂H₂₄O₂.

Dithymoxylethane, CH₃—CH(C₁₀H₁₂OH)₂, crystallizes in rounded plates, melting at 180° C. (356° F.), soluble in most of the usual solvents, except water.

Dithymoxylethene, CH₂=C(C₁₀H₁₂OH)₂, forms needle-shaped crystals, melting at 170°–171° C. (338°–339.8° F.), insoluble in water, rather more soluble than the preceding in other solvents. Treated with weak oxidizing agents, as with potassium ferrocyanide in dilute alcoholic solution, it forms green crystals, C₄₄H₅₄O₄, melting at 214°–215° C. (417.2°–419° F.), soluble in toluene and in chloroform; but if the solution be previously rendered alkaline, a red precipitate is formed, which dissolves in chloroform and separates therefrom in red crystals, melting at 215° C. (419° F.), and having the composition C₂₂H₂₄O₂.

A mixture of dithymoxylethene and the red crystals dissolved in chloroform deposits, on evaporation, the above-described green needles: C₂₂H₂₄O₂ + C₂₂H₂₆O₂ = C₄₄H₅₄O₄. Hence it appears that dithymoxylethene and the two products of its oxidation are related to one another in the same manner as hydroquinone, quinhydrone, and quinone, thus:



* This compound, and those which follow it, were discovered by Dr. E. Jäger (Deutsch. Chem. Ges. Ber. 1874, 1197; Chem. Soc. Journ. 1877, 262), who designates them, not as thymoxyl-compounds, but as thymyl-compounds; but the name "dithymylethane" belongs properly, not to a phenol, but to the hydrocarbon C₂₂H₂₆ = (C₁₁H₇—CH(C₁₀H₁₂))₂, homologous with diphenyl-ethane and ditolyl-ethane; and so of the rest.

Alcohols.

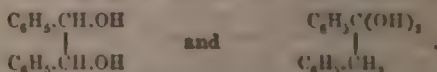
Benzhydrol, $C_{15}H_{14}O = C_6H_5-CH(OH)-C_6H_5$, is obtained by the action of sodium-amalgam on a solution of benzophenone in dilute alcohol. It crystallizes in needles, melts at $68^\circ C.$ ($154.4^\circ F.$), and boils at $288^\circ C.$ ($568.4^\circ F.$), with partial decomposition into water and benzhydrol ether, $[(C_6H_5)_2CH]_2O$.

Toluylene Hydrate or Stilbene Hydrate, $C_{14}H_{12}O = C_6H_5-CH_2-CH(OH)-C_6H_5$, is formed by the action of sodium-amalgam on deoxybenzoin, $C_{14}H_{12}O$ (p. 942), and by heating deoxybenzoin or hydrobenzoin with alcoholic potash. Long, slender, brittle needles, having a vitreous lustre, melting at $62^\circ C.$ ($143.6^\circ F.$); insoluble in water, easily soluble in alcohol and ether. Resolved by boiling with dilute sulphuric acid into stilbene and water; oxidized by nitric acid to deoxybenzoin; reduced by H_2 to dibenzyl. With acetyl chloride, it forms toluylene acetate, $C_{16}H_{16}O_2$, which is a viscid liquid.

Dimethyl-benzhydrol, $C_{15}H_{16}O = CHOH(C_6H_4-CH_3)_2$, obtained by the action of sodium-amalgam on ditolylketone in alcoholic solution forms slender needles melting at $69^\circ C.$ ($156.2^\circ F.$).

Triphenyl carbinol $C_{18}H_{15}O = (C_6H_5)_3C(OH)$, from triphenyl-methane by oxidation with chromic acid mixture, forms monoclinic crystals, melts at $157^\circ C.$ ($314.6^\circ F.$), boils without decomposition above $322^\circ C.$ ($652^\circ F.$). Its solution in benzene heated with P_2O_5 yields triphenyl-methane and dibenzyl.

Tolylene Glycols, $C_{14}H_{14}O_2$.—Two diatomic alcohols of this composition, called *Hydrobenzoin* and *Ischydrobenzoin*, are formed by the action of zinc and hydrochloric acid on benzaldehyde; also by that of sodium-amalgam on the same compound in alcoholic solution. By oxidation with chromic acid mixture both of them are converted into benzaldehyde and benzoic acid: consequently they must be represented by the formulæ:



Now one of them (hydrobenzoin) is the sole product of the action of sodium-amalgam on benzil, $C_6H_5-CO-CO-C_6H_5$; this, therefore, must be represented by the left hand or symmetrical formula; and ischydrobenzoin, if not a mere physical modification, by the unsymmetrical formula. By the action of PBr_3 , both compounds are converted into tolylene dibromide, $C_7H_6Br_2$.

Hydrobenzoin is sparingly soluble in water, easily in alcohol, and crystallizes in large rhombic plates, melting at $132.5^\circ C.$ ($270.5^\circ F.$), and subliming without decomposition. By heating with strong nitric acid it is converted into benzoin. Its acetylic ether, $C_{16}H_{16}(OC_2H_5O)_2$, forms large prisms melting at $133^\circ-134^\circ C.$ ($271.4^\circ-273.2^\circ F.$).

Ischydrobenzoin crystallizes from water in long, shining, six-sided hydrated prisms, which effloresce on exposure to the air, from alcohol in anhydrous monoclinic prisms. It melts at $119.5^\circ C.$ ($247.1^\circ F.$), is more soluble in alcohol than hydrobenzoin; is not converted into benzoin by nitric acid.

Fluorenyl Alcohol, $C_{15}H_{12}O = \begin{array}{c} C_6H_5 \\ | \\ C_6H_4 \\ | \end{array} > CH.OH$, produced by the

action of sodium-amalgam on an alcoholic solution of diphenylene ketone, forms colorless hexagonal laminæ, melting at $153^\circ C.$ ($307.4^\circ F.$).

Ketones.

Diphenyl Ketone or Benzophenone, $C_6H_5.CO.C_6H_5$, is formed by oxidation of diphenyl-methane and diphenyl-ethane (p. 564) with chromic acid mixture; by heating mercury-diphenyl (p. 845) with benzoyl chloride; and most readily (together with benzene) by distillation of calcium benzoate. It usually crystallizes in large rhombic prisms melting at $48^\circ-49^\circ C.$ ($118.4^\circ-120.2^\circ F.$), sometimes also in rhombohedrons melting at $27^\circ C.$ ($80.6^\circ F.$); the latter modification is converted on standing into the former. It has an aromatic odor, boils at $295^\circ C.$ ($563^\circ F.$), dissolves easily in alcohol. Treated with PCl_5 , it is converted into benzophenonic chloride, $(C_6H_5)_2CCl_2$, a liquid boiling at about $300^\circ C.$ ($572^\circ F.$). Sodium-amalgam converts it into benzhydrol (p. 940).

Phenyl-tolyl Ketone, $C_{14}H_{12}O = C_6H_5.CO.C_6H_4(CH_3)$, is obtained in two modifications by oxidation of benzyl-toluene; by heating a mixture of benzoic acid and toluene with P_2O_5 ; by heating a mixture of calcium benzoate and paratoluate; and by heating benzyl chloride and toluene with zinc-dust. The *a*-compound (para) exists in two dimorphous modifications—one, hexagonal, melting at $55^\circ C.$ ($131^\circ F.$); the other, monoclinic, melting at $59^\circ-60^\circ C.$ ($138.2^\circ-140^\circ F.$). Boiling point, $310^\circ-312^\circ C.$ ($590^\circ-593.6^\circ F.$). Heated with soda-lime it yields benzene and paratoluic acid. The *B*-compound, which is liquid, has not been obtained pure. By distillation with zinc-dust, it yields anthracene; with lead oxide, anthraquinone: the *a*-compound does not yield these products.

Titolyl Ketone, $CO(C_6H_4.CH_3)_2$, forms rhombic crystals melting at $95^\circ C.$ ($203^\circ F.$).

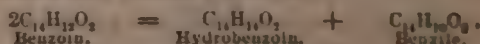
Dibenzyl Ketone, $CO(CH_2.C_6H_5)_2$, obtained by distillation of calcium *a*-toluato, forms colorless crystals, m. p. $30^\circ C.$ ($86^\circ F.$), b. p. $320^\circ-321^\circ C.$ ($608^\circ-609.8^\circ F.$); yields by oxidation benzoic and carbonic acids.

Diphenylene Ketone, $C_{12}H_8O = CO \begin{array}{c} < C_6H_5 \\ < C_6H_5 \end{array}$, obtained by heating di-

phenic acid or phenyl-benzoic acid (p. 942) with lime, also by oxidizing fluorene with chromic acid mixture, forms large yellow rhombic crystals, melts at $84^\circ C.$ ($183.2^\circ F.$), boils at $336^\circ-338^\circ C.$ ($636.8^\circ-639.6^\circ F.$); is converted by reducing agents into fluorene, by fusion with potash into phenyl-benzoic acid.

Benzoin, $C_{14}H_{12}O_2 = C_6H_5.CO.CH(OH).C_6H_5$, formed by heating hydrobenzoin with nitric acid (specific gravity 1.4), and by mixing bitter-almond oil with a concentrated alcoholic solution of potassium cyanide, crystallizes in shining prisms melting at $133^\circ-134^\circ C.$ ($271.4^\circ-273.2^\circ F.$); dissolves sparingly in water and in cold alcohol or ether, freely in hot alcohol. Converted by chromic acid mixture into benzaldehyde and benzoic acid; by heating with fuming hydriodic acid into dibenzyl; by heating

with alcoholic potash, into hydrobenzoin and benzile, together with benzoic acid, benzoic acid, and other products:



With acetyl chloride it yields acetyl-benzoin, $C_{14}H_{14}(C_2H_3O)_2$, which forms crystals melting at $75^\circ C.$ ($167^\circ F.$).

Deoxybenzoin, or Phenyl-benzyl Ketone, $C_{14}H_{12}O = C_6H_5.CO.CH_2(C_6H_5)$, is formed by the action of zinc and hydrochloric acid on benzoin and chlorobenzile; by heating monobromostilbene with water to $180-190^\circ C.$ ($356-374^\circ F.$), and by distillation of a mixture of benzoate and *o*-toluate of calcium:



It crystallizes from alcohol in large plates melting at $56^\circ C.$ ($131^\circ F.$), sublimes without decomposition; is converted by sodium-amalgam into toluylene hydrate (p. 940), by PCl_5 into monochlorotoluylene, and by heating with hydriodic acid into benzile.

Benzile, $C_{14}H_{10}O_2 = C_6H_5.CO.CO.C_6H_5$ (*Dibenzoyl*), is formed by oxidation of benzoin with nitric acid or chlorine, and, together with stilbene, by heating stilbene bromide with water and silver oxide. It crystallizes in large six-sided prisms, melting at $90^\circ C.$ ($194^\circ F.$), insoluble in water, soluble in alcohol and ether. By oxidation with chromic acid mixture, it is converted into benzoic acid; by nascent hydrogen (zinc and HCl , or iron filings and acetic acid) into benzoin; by heating with PCl_5 into benzile chloride, $C_{14}H_{10}Cl_2O$, or $C_6H_5.CCl_2.CO.C_6H_5$, which crystallizes in rhombic prisms melting at $71^\circ C.$ ($159.8^\circ F.$), and is converted by zinc and HCl into deoxybenzoin. Benzile and its chloride, heated to $200^\circ C.$ ($392^\circ F.$) with PCl_5 , yield toluene tetrachloride, $C_{14}H_{10}Cl_4$.

Acids.

Diphenylcarbonic Acid, $C_{12}H_{10}O_4 = C_6H_5.C_6H_4.CO_2H$ (1 : 4), is produced by heating cyanodiphenyl, $C_{12}H_9(CN)_2$, with alcoholic potash (p. 934), or by oxidizing diphenyl-benzene (p. 936) dissolved in glacial acetic acid with chromic anhydride. It crystallizes from alcohol in tufts of needles; melts at $218-219^\circ C.$ ($424.4-426.2^\circ F.$); is converted by heating with lime into diphenyl, and by oxidation with chromic acid into terephthalic acid.

Phenyl-benzoic acid, $C_{13}H_{10}O_4 = C_6H_5.C_6H_4.CO_2H$ (1 : 2), produced by the action of melting potash on diphenylene ketone (p. 941) forms lamellar crystals, melting at $110-111^\circ C.$ ($230-231.8^\circ F.$), reconverted into diphenylene ketone by heating with lime.

Diphenyl-dicarbonic Acid, $C_{12}H_{10}O_6 = C_6H_5(CO_2H)_2$ (*para*), from dicyanodiphenyl, $C_{12}H_9(CN)_2$, is a white amorphous powder, insoluble in alcohol and ether, neither fusible nor sublimable. Heated with lime it yields diphenyl. Its barium and calcium salts are nearly insoluble in water. The diethyl ether melts at $112^\circ C.$ ($233.6^\circ F.$).

Diphenic acid, isomeric with the last, is formed by oxidation of phenanthrene or phenanthrene quinone with chromic acid mixture. It melts at $220^\circ C.$ ($438.8^\circ F.$), sublimes in needles, dissolves very easily in alcohol.

and ether. The barium and calcium salts are easily soluble in water; the diethyl ether is liquid.

Diphenylacetic Acid, $C_{15}H_{12}O_2 = (C_6H_5)_2CH.CO.OH$, is formed by heating benzoic acid with hydriodic acid to $150^\circ C.$ ($302^\circ F.$), and by heating a mixture of phenyl-bromacetic acid and benzene with zinc-dust:



It crystallizes from water in slender needles, from alcohol in laminæ, and melts at $146^\circ C.$ ($294.8^\circ F.$); is converted by chromic acid mixture into diphenyl ketone; by heating with soda-lime into diphenyl-methane.

Diphenyl-glycollic or Benzoic Acid, $C_{14}H_{10}O_3 = (C_6H_5)_2C(OH).CO_2H$, is formed by passing bromine-vapor into diphenyl-acetic acid, and boiling the product with water; also by heating benzene with alcoholic potash (not in excess); in this reaction, a transposition of atoms must take place. It crystallizes in shining needles or prisms, easily soluble in hot water and in alcohol; melts at $150^\circ C.$ ($302^\circ F.$), turning red at the same time. It dissolves with dark red color in sulphuric acid. By heating with HI, it is converted into diphenyl-acetic acid; by oxidation into diphenyl ketone; by distillation of its barium salts into benzhydrol (p. 940).

Benzoyl-benzoic Acids, $C_{14}H_{10}O_3 = C_6H_5.CO.C_6H_4.CO_2H$.—The *para*-modification is formed by oxidation of solid phenyltolyl ketone, *para*-benzyl-benzoic acid, benzyl-toluene, benzylethyl-benzene, and ethylbenzyl-toluene (p. 930), with chromic acid mixture. It sublimes in laminæ, resembling benzoic acid, and melts at $194^\circ C.$ ($381.2^\circ F.$). The *ortho*-modification, from liquid phenyl-tolyl ketone, crystallizes from hot water in needles or prisms containing $1H_2O$. The crystals melt at $86^\circ-87^\circ C.$ ($185^\circ-188.6^\circ F.$); the anhydrous acid at $127^\circ-128^\circ C.$ ($260.6^\circ-262.4^\circ F.$).

Benzhydryl-benzoic acids, $C_6H_5.CH(OH).C_6H_4.CO_2H$.—The *para*-acid, formed by the action of nascent hydrogen on *para*-benzyl-benzoic acid, crystallizes in needles, melts at $164^\circ-165^\circ C.$ ($327.2^\circ-329^\circ F.$), and is reconverted by oxidation into *para*-benzoylbenzoic acid. The *ortho*-acid cannot be obtained in the free state, as on attempting to prepare it by the action of nascent hydrogen on *ortho*-benzylbenzoic acid, it splits up into water and the anhydride $C_{14}H_{10}O_2$. This compound crystallizes from alcohol or ether in prisms melting at $115^\circ C.$ ($239^\circ F.$); is converted by oxidation into *ortho*-benzylbenzoic acid, and by PCl_5 into anthraquinone and chlorinated compounds.

Benzyl-benzoic acid, $C_{14}H_{12}O_2 = C_6H_5.CH_2.C_6H_4.CO_2H$.—The *para*-acid is obtained by the prolonged action of HI and phosphorus at $160^\circ-170^\circ C.$ ($320^\circ-336^\circ F.$) on *para*-benzoyl- or benzhydryl-benzoic acid. Laminæ or needles, melting at $157^\circ C.$ ($314.6^\circ F.$). The *ortho* acid, obtained in like manner from *ortho*-benzoyl-benzoic acid, forms slender shining needles, melting at $114^\circ C.$ ($237.2^\circ F.$)

NAPHTHALENE GROUP.

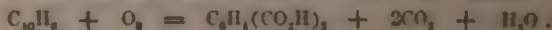
Naphthalene, $C_{10}H_8$.—This hydrocarbon is produced in the decomposition of toluene, xylene, and cumene at a red heat (p. 816), also by passing vapor of benzene, cinnamene, chrysene, or anthracene through a

red-hot tube. It is formed in large quantities as a bye-product in the preparation of coal-gas, its production doubtless arising from reactions similar to those just mentioned. When the last portion of the volatile oily product which passes over in the distillation of coal-tar is collected apart and left to stand, a quantity of solid crystalline matter separates, which is principally naphthalene. An additional quantity may be obtained by pushing the distillation until the contents of the vessel begin to char: the naphthalene then condenses in the solid state, but dark-colored and very impure. By simple sublimation, once or twice repeated, it is obtained perfectly white.

Naphthalene is formed synthetically from phenyl-butylene, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH \cdot CH_3$, which is obtained by the action of sodium on a mixture of benzyl chloride, $C_6H_5 \cdot CH_2 \cdot Cl$, and allyl iodide, $CH_2 \cdot CH \cdot CH_3$. This hydrocarbon or its bromide passed through a red-hot tube filled with lime, is resolved into naphthalene and hydrogen, $C_{10}H_{12} = C_{10}H_8 + 2H_2$. Naphthalene forms large colorless, transparent, brilliant, crystalline plates, exhaling a faint and peculiar odor. It melts at $79.2^\circ C.$ ($174.6^\circ F.$) as a clear, colorless liquid, which crystallizes on cooling; boils at $218^\circ C.$ ($424.4^\circ F.$). When strongly heated in the air, it takes fire, and burns with a red and very smoky flame. It is insoluble in cold water, but soluble to a slight degree at the boiling heat; alcohol and ether dissolve it easily; a hot saturated alcoholic solution deposits fine iridescent crystals on cooling. It unites with *picric acid*, forming the compound $C_{10}H_8 \cdot C_6H_2(NO_2)_3O$, which crystallizes in stellate groups of needles.

Naphthalene, like benzene and its homologues, forms addition-products with hydrogen and chlorine. Heated with PH_3 to $190^\circ C.$ ($374^\circ F.$) or with HI and amorphous phosphorus to 220° – $250^\circ C.$ (428° – $482^\circ F.$), it forms the tetrahydride, $C_{10}H_{12} \cdot H_4$, a pungent liquid boiling at $206^\circ C.$ ($401^\circ F.$). With chlorine, it forms the compound, $C_{10}H_8 \cdot Cl_2$, which is a pale yellow oil, and $C_{10}H_8 \cdot Cl_4$, $C_{10}H_8 \cdot Cl_2 \cdot Cl_2$, and $C_{10}H_8 \cdot Cl_4 \cdot Cl_2$, which crystallizes in monoclinic prisms, melting respectively at $182^\circ C.$ ($359.6^\circ F.$), 128° – $130^\circ C.$ (262.4° – $266^\circ F.$), and $172^\circ C.$ ($341.6^\circ F.$).

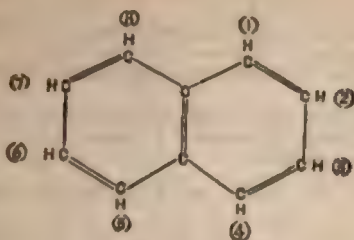
The structure of the naphthalene molecule is deduced by Gräbe (*Liebig's Annalen*, cxlix. 26) from the following considerations. Naphthalene is converted by oxidation into phthalic or benzene-dicarboxylic acid, $C_6H_4(CO_2H)_2$, two of its carbon-atoms being removed as carbon dioxide, while two others remain in the form of carboxyl:



Hence naphthalene contains a benzene-residue, C_6H_4 , and may be represented by the formula $C_6H_4 \cdot C_4H_4$. The same conclusion follows from the synthesis of naphthalene from phenyl-butylene. But phthalic acid is likewise produced by oxidation of dichloronaphthoquinone, $C_{10}H_6Cl_2O_2$; consequently, this compound has its two chlorine-atoms and two oxygen-atoms associated with the four carbon-atoms which undergo oxidation, and may be represented by the formula $C_6H_4 \cdot C_4Cl_2O_2$. By the action of phosphorus pentachloride, the two oxygen-atoms are replaced by two chlorine-atoms, and at the same time one of the four hydrogen-atoms is replaced by chlorine, the result being pentachloronaphthalene, $C_{10}H_5Cl(Cl_4)$ ($C_6H_4 \cdot C_4Cl_5$), which is converted by oxidation into tetrachlorophthalic acid, $C_6H_2Cl_4(CO_2H)_2$. In this reaction, therefore, two of the carbon-atoms belonging to the left-hand group in the molecule $C_{10}H_5Cl(Cl_4)$ are removed as carbon dioxide, while two others yield the two groups CO_2H and the remaining two, together with the four standing on the right, form the benzene-nucleus, $C_6H_2Cl_4$, of tetrachlorophthalic acid.

These transformations show that the molecule of naphthalene is sym-

metrical, and composed of two benzene-nuclei united in the manner represented by the following figure:—



The replacement of the hydrogen-atoms in naphthalene by other elements and by compound radicles gives rise to numerous substitution-derivatives, which are obtained by methods similar to those by which the benzene-derivatives are produced. The number of possible isomerides among the naphthalene-derivatives is, however, much greater than those of the benzene-derivatives. Thus, the mono-derivatives of benzene do not admit of isomeric modifications, but in naphthalene the places 1, 4, 5, 8 (see the preceding figure), though similar to each other, are different from the places 2, 3, 6, 7, which are likewise similar amongst themselves. Hence, there will be two modifications of each mono-derivative of naphthalene (chloro-, nitro-, etc.). Those modifications in which the substituted radicle occupies the place 1 (= 4, 5, or 8), are called α -derivatives; those in which it is placed at 2, 3, 6, 7, are called β -derivatives. The di-derivatives, $C_{10}H_8X_2$, exhibit ten isomeric modifications, according as the substituted radicles are situated: (1) in the same benzene-ring (1 : 2, 1 : 3, 1 : 4, or 5 : 6, 5 : 7, 5 : 8, and 2 : 3, or 6 : 7), secondly, in different rings (1 : 5, 1 : 6, 1 : 7, 1 : 8, 2 : 6, and 2 : 7). The list of actually known modifications is, however, very incomplete.*

Chloronaphthalenes are obtained by boiling the chlorides of naphthalene with alcoholic potash, which removes HCl ; these, when subjected to the action of chlorine, also form addition-products such as $C_{10}H_7Cl_2Cl_2$; and from these, by the action of alcoholic potash, more highly chlorinated substitution-derivatives may be obtained.

Monochloronaphthalenes, $C_{10}H_7Cl$.— α , from naphthalene dichloride, is a liquid boiling at $250^\circ C.$ ($482^\circ F.$).— β , By the action of PCl_5 on β -naphthol. Colorless crystalline mass, m. p. $60^\circ C.$ ($140^\circ F.$); b. p. 256° – $258^\circ C.$ (492.8° – $496.4^\circ F.$).

$C_{10}H_6Cl_2$ is known in seven, and $C_{10}H_5Cl_3$, in four modifications. $C_{10}Cl_{10}$, the final product of the action of chlorine on naphthalene, forms prisms melting at $135^\circ C.$ ($275^\circ F.$).

Of monobromonaphthalene, two modifications are known, one formed by direct bromination, being a liquid boiling at $277^\circ C.$ ($530.6^\circ F.$); the other from β -naphthylamine by the diazo-reaction with alcohol, forming white shining laminae, melting at $68^\circ C.$ ($154.4^\circ F.$).

Iodonaphthalene, $C_{10}H_7I$, produced by the action of iodine on mercuro naphthide, is an oil boiling at $300^\circ C.$ ($572^\circ F.$).

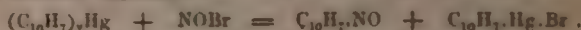
Cyanonaphthalenes, or Naphthyl Cyanides, $C_{10}H_7CN$ (α and β), are formed by distilling the potassium salts of the corresponding

* For the latest researches on naphthalene derivatives, see Liebermann (Liebig's *Annalen*, clxxxiii 225), and Atterberg (*Deutsch. Chem. Ges. Ber.*, 1870, pp. 1730, 1734).

naphthalenesulphonic acids with potassium cyanide.—*a*. Crystallizes in needles, melts at 37.5°C . (99.5°F .), and boils at 297°C . (566.6°F .).—*b*. Forms laminae, melts at 66.5°C . (149.9°F .), boils at 304°C . (579.2°F .).

Dicyanonaphthalenes, $\text{C}_{10}\text{H}_6(\text{CN})_2$, are formed in like manner from the naphthalene-disulphonic acids.—*a*. Needles melting at 297°C . (566.6°F .).—*b*. Needles melting at 290°C . (554.2°F .).

Nitrosonaphthalene, $\text{C}_{10}\text{H}_7\text{NO}$, is formed by the action of nitrogen oxybromide, NOBr (solution of NO and Br in CS_2 at -20°C ., — F .), on mercuric naphthide:



It separates from solution in benzene or light petroleum in yellow nodules, turning red in contact with the air; melts at 85°C . (185°F .) and decomposes at 134°C . (273.2°F .). Its solution in phenol is colored blue by sulphuric acid.

Nitronaphthalene, $\text{C}_{10}\text{H}_7\text{NO}_2$, obtained by heating a solution of naphthalene in glacial acetic acid with ordinary nitric acid for half an hour, crystallizes from alcohol in sulphur-yellow prisms, melts at 61°C . (141.8°F .), boils at 304°C . (579.2°F .); insoluble in alcohol, ether, and carbon sulphide.

Two dinitronaphthalenes are obtained by boiling naphthalene or mononitronaphthalene with nitric acid till the oily liquid which forms on the surface has disappeared.—*a*. Colorless prisms melting at 214°C . (415.4°F .).—*b*. Rhombic plates melting at 170°C . (338°F .).

These compounds, boiled with fuming nitric acid, yield three trinitronaphthalenes, boiling respectively at 122° , 147° , and 219°C . (251.6° , 296.6° , 424.4°F .); and on further boiling, two tetranitronaphthalenes, melting at 200° and 259°C . (392° , 498.2°F .).

Amidonaphthalenes or Naphthylamines, $\text{C}_{10}\text{H}_7\text{NH}_2$.—The *a*-isomer obtained by reduction of nitronaphthalene, crystallizes in needles or prisms, easily soluble in alcohol; has a pungent odor; melts at 37°C . (122°F .), and boils at 300°C . (572°F .). It forms easily soluble crystalline salts, the solutions of which give with chromic acid or ferric chloride, a blue precipitate, quickly changing to a purple-red powder of *arylnaphthylamine*, $\text{C}_{10}\text{H}_7\text{NO}$. *a*-Naphthylamine, heated with glacial acetic acid, yields *a*-Acetonaphthalide, $\text{C}_{10}\text{H}_7\text{NH}(\text{C}_2\text{H}_3\text{O})$, which crystallizes in fine silky fibres, melting at 159°C . (318.2°F .).

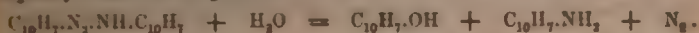
b-Naphthylamine is obtained from bromonitronaphthylamine, which is formed by nitration of bromoacetonaphthalide, $\text{C}_{10}\text{H}_6\text{Br.NH}(\text{C}_2\text{H}_3\text{O})$. The amido-group is eliminated by the action of nitrous acid and alcohol, and the resulting bromonitronaphthalene is reduced by tin and hydrochloric acid. *b*-Naphthylamine forms nacreous laminae melting at 113°C . (233.6°F .).

Nitronaphthylamine, $\text{C}_{10}\text{H}_6\text{NO}_2\text{NH}_2$, obtained by reduction of *a*-nitronaphthalene, forms small red crystals melting at 118°C . (244.4°F .). Two isomeric nitronaphthylamines melting at 191° and 188°C . (376.8° , 314.4°C – 318.2°F .) are formed by the nitration of the acetyl-compound, which melts at 159°C . (318.2°F .).

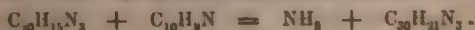
Diamidonaphthalene or Naphthylenediamine, from nitronaphthylamine (m. p. 191°C ., 376.8°F .), is converted by oxidation with dilute chromic acid into naphthoquinone. Two other naphthylenediamines are obtained by reduction of dinitronaphthalenes.

The naphthylamines treated with nitrous acid yield diazo-compounds, analogous to those obtained from aniline.

Diazo-amidonaphthalene, $C_{20}H_{15}N_3 = C_{10}H_7.N_2.NH(C_{10}H_7)$, obtained by the action of nitrous acid on a cold alcoholic solution of naphthylamine, forms brown laminae, and is resolved by heating with acids into naphthylamine and naphthol:



The action of nitrous acid on a warm alcoholic solution of naphthylamine, or of potassium nitrite on its solution in hydrochloric acid, produces amidazonaphthalene, $C_{10}H_7.N_2.C_{10}H_6.NH_2$, metameric with diazo-amidonaphthalene, and analogous to amidazobenzene (p. 852). It dissolves easily in alcohol, and crystallizes in orange-red needles having a green metallic lustre. Its salts are violet-colored. Heated with naphthylamine it forms a base, $C_{20}H_{21}N_3$, analogous to rosaniline:



The hydrochloride of this base, $C_{20}H_{21}N_3.HCl + H_2O$, forms the fine red dye-stuff called *Naphthalene-red* or *Magentha-red*. It crystallizes in green metallically lustrous needles, and dissolves in alcohol, forming a red solution, which when dilute exhibits a beautiful fluorescence.

Mercuric Naphthide, $(C_{10}H_7)_2Hg$, produced by the action of sodium-amalgam on a solution of bromonaphthalene in benzene, forms shining crystals, easily soluble in hot benzene, sparingly in alcohol and ether. It melts at $243^\circ C.$ ($469.4^\circ F.$), and decomposes partially when sublimed. Haloid acids decompose it into naphthalene and mercury-salts. It unites with iodine, forming the compound $(C_{10}H_7)_2HgI_2$, which is decomposed by a larger quantity of iodine, thus:



Heated with soda-lime it yields dinaphthyl and naphthalene.

Naphthalene-sulphonic Acids, $C_{10}H_7.SO_3H$, α and β , are formed by gradually heating naphthalene with sulphuric acid, and may be separated by fractional crystallization of their barium or lead-salts, those of the α -acid being much more soluble in water and alcohol than the β -salts. The free acids are crystalline and deliquescent. The α -acid is converted by heat into the β -acid: the latter is therefore almost the sole product obtained at a high temperature ($150^\circ C.$, $320^\circ F.$). The α -acid, heated with dilute hydrochloric acid to 200° , is resolved into naphthalene and sulphuric acid. The chlorides, $C_{10}H_7.SO_2Cl$, are obtained by heating the potassium salts with PCl_5 . They crystallize in shining laminae, α more soluble in ether than β . The α -chloride melts at $66^\circ C.$ ($150.8^\circ F.$); β at $76^\circ C.$ ($168.8^\circ F.$). By zinc and sulphuric acid they are converted into mercaptans, $C_{10}H_7.SH$.

By prolonged heating of naphthalene with sulphuric acid, two *naphthalene-sulphonic acids*, $C_{10}H_6(SO_3H)_2$, are formed, which when distilled with KCN yield the corresponding *dicyanides*, $C_{10}H_6(CN)_2$.

Naphthols, $C_{10}H_7.OH$, are formed by fusing the two monosulphonic acids with potash.

α -Naphthol is also produced by boiling the aqueous solution of diazo-naphthalene nitrate (from α -naphthylamine) with nitrous acid. It crystallizes in colorless monoclinic prisms, melts at $94^\circ C.$ ($201.2^\circ F.$), boils at $277-250^\circ C.$ ($532.4-536^\circ F.$); is nearly insoluble in cold water, somewhat more soluble in hot water, easily in alcohol and ether. Ferric chloride and bleaching powder give to the aqueous solution a transient violet color.

With alkalis, etc., α -naphthol forms derivatives exactly like those of phenol. The *ethylic ether*, $C_{10}H_7 \cdot O \cdot C_2H_5$, is a colorless liquid, boiling at $272^\circ C.$ ($521.6^\circ F.$), not solidifying at $-5^\circ C.$ ($23^\circ F.$). *α -Acetyl naphthol*, $C_{10}H_7 \cdot O \cdot C_2H_3O$, formed by the action of acetyl chloride, is a yellowish liquid, insoluble in water. The *benzoyl* derivative melts at $56^\circ C.$ ($132.8^\circ F.$).

Nitro- α -naphthol, $C_{10}H_6 \left\{ \begin{array}{l} OH \\ N(O)_2 \end{array} \right.$ (1 : 4) obtained by boiling nitronaphthylamine (m. p. $191^\circ C.$, $375.8^\circ F.$) with potash, crystallizes from alcohol in lemon-yellow capillary needles; from acetic acid or acetone in golden-yellow prisms; melts at $164^\circ C.$ ($327.2^\circ F.$). Its sodium salt is a yellow dye-stuff called *Campobello yellow*. By reduction with tin and HCl, it yields amido- α -naphthol, which, by boiling with bromine-water or by the action of nitrous acid, is converted into naphthoquinone.

An isomeric nitro- α -naphthol, formed from the nitronaphthylamine melting at 158° – $159^\circ C.$ (316.4° – $318.2^\circ F.$), crystallizes in greenish-yellow laminae, melting at $128^\circ C.$ ($262.4^\circ F.$), much less soluble in alcohol than the preceding.

Dinitro- α -naphthol, $C_{10}H_5(NO_2)_2OH$, is formed by mixing α -naphthylamine with 4–6 parts of strong nitric acid; by boiling diazonaphthalene hydrochloride with nitric acid; or by gently heating a solution of α -naphthalene-sulphonic acid with nitric acid. Shining sulphur-yellow crystals, melting at $138^\circ C.$ ($280.2^\circ F.$), sparingly soluble in alcohol and ether, more freely in chloroform. It forms salts with bases, and decomposes carbonates. Its calcium and sodium salts form splendid yellow dyes, known as *naphthalene-yellows*.

Dinitronaphthol treated with zinc and hydrochloric acid yields the hydrochloride of *diamidonaphthol*, $C_{10}H_5(NH_2)_2 \cdot OH$, the aqueous solution of which is converted by exposure to the air, or by the action of ferric chloride, into the hydrochloride of *di-imidonaphthol*, $C_{10}H_4(OH) \left\langle \begin{array}{c} NH \\ NH \end{array} \right\rangle$.

β -Naphthol or *Isonaphthol*, $C_{10}H_7 \cdot OH$, from β -naphthalene-sulphonic acid, crystallizes in small rhombic tables, melts at $122^\circ C.$ ($251.6^\circ F.$), boils at 285° – $290^\circ C.$ (545° – $554^\circ F.$), and sublimes with great facility; dissolves sparingly in boiling water, easily in alcohol and ether. The *ethylic ether*, $C_{10}H_7 \cdot O \cdot C_2H_5$, melts at $33^\circ C.$ ($91.4^\circ F.$), the acetyl-compound at $60^\circ C.$ ($140^\circ F.$), the benzyl-compound at $107^\circ C.$ ($224.6^\circ F.$).

Dinitro- β -naphthol, obtained by heating the alcoholic solution of β -naphthol with dilute nitric acid, forms yellow needles melting at $195^\circ C.$ ($383^\circ F.$).

Diorynaphthalene or *Naphthohydroquinone*, $C_{10}H_6(OH)_2$ (1 : 4), is formed from naphthoquinone by heating with hydriodic acid and amorphous phosphorus. It crystallizes from hot water in long colorless needles, melting at $176^\circ C.$ ($348.8^\circ F.$), converted by oxidation into naphthoquinone. An isomeric compound, obtained from naphthalene-disulphonic acid, forms needles slightly soluble in water.

Naphthoquinone, $C_{10}H_6 \left\langle \begin{array}{c} O \\ O \end{array} \right\rangle$, is formed by oxidation of naphthalene with chromic anhydride dissolved in glacial acetic acid, more readily by adding a dilute aqueous solution of chromic acid to a solution of diamido-naphthalene hydrochloride (p. 947); on distilling the liquid, the naphthoquinone passes over with the steam. Large sulphur-yellow trielinic tables, having a pungent odor, melting at $125^\circ C.$ ($257^\circ F.$), subliming below 100° ; insoluble in cold water, slightly soluble in cold alcohol, easily in hot alcohol and in ether. Converted by oxidation with nitric acid into phthalic acid.

Dichloronaphthoquinone, $C_{10}H_4Cl_2O_2$, is formed by heating α -naphthol or dinitronaphthol (commercial naphthalene yellow) with potassium chlorate and hydrochloric acid; also by the action of chromyl chloride, CrO_2Cl_2 , on a solution of naphthalene in glacial acetic acid. Crystallizes in golden-yellow needles melting at $189^\circ C.$ ($372.2^\circ F.$); oxidized by nitric acid to phthalic acid; converted by PCl_5 into $C_{10}H_4Cl_2$, which oxidizes to chlorophthalic acid. Boiled with soda-lye, it dissolves with red color, forming the sodium salt of chloronaphthalic acid, $C_{10}H_3Cl(O_2)OH$, which crystallizes in yellow needles, melting at $200^\circ C.$ ($392^\circ F.$).

Oxynaphthoquinone or *Naphthalenic acid*, $C_{10}H_6(OH)\langle \text{O} \rangle$, is formed from the hydrochloride of di-imidonaphthol (p. 948) by heating with dilute hydrochloric acid to $120^\circ C.$ ($248^\circ F.$).



Light yellow, strongly electric powder, or yellow needles; sparingly soluble in hot water, easily in alcohol and ether; unites with nascent hydrogen, forming trioxynaphthalene. It is a rather strong monobasic acid, capable of decomposing carbonates. Its alkali-salts are blood-red, and easily soluble in water.

Dioxynaphthoquinone or *Naphthazarin*, $C_{10}H_4(O_2)(OH)_2$.—This compound is a dye-stuff very much like alizarin. It is obtained by gradually adding dinitronaphthol (4 parts), and granulated zinc ($\frac{1}{2}$ –1 part), to a mixture of strong sulphuric acid (40 parts), and fuming sulphuric acid (4 parts) heated to $200^\circ C.$ ($392^\circ F.$) (not above $205^\circ C.$, $401^\circ F.$). On diluting the mixture with water, boiling, and filtering, the naphthazarin separates as a red gelatinous mass, which may be purified by sublimation. Long needles having a splendid green metallic lustre, dissolving in alcohol with red, in ammonia with sky-blue color. The solutions give violet-blue precipitates with baryta- and lime-water, crimson with alum.

Naphthoic Acids, $C_{10}H_7CO_2H$.— α -Naphthoic acid is obtained from α -cyanonaphthalene (p. 945); also by fusing potassium α -naphthalenesulphonate with sodium formate, and by the action of sodium-amalgam on a mixture of bromonaphthalene and ethyl chlorocarbonate. Slender needles melting at $160^\circ C.$ ($320^\circ F.$), slightly soluble in hot water, easily in hot alcohol. By distillation with baryta it is resolved into naphthalene and carbon dioxide. Its *ethylic ether* boils at $309^\circ C.$ ($588.2^\circ F.$); the *chloride*, $C_{10}H_7COCl$, at $297^\circ C.$ ($566.6^\circ F.$).

β -Naphthoic or *Isonaphthoic acid*, from β -cyanonaphthalene, crystallizes from hot water in long silky needles melting at $182^\circ C.$ ($359.6^\circ F.$).

Oxynaphthoic acids, $C_{10}H_6\begin{smallmatrix} OH \\ CO_2H \end{smallmatrix}$, are formed from the two naphthols by the action of sodium and carbon dioxide. The α -acid melts at $185^\circ C.$ ($365^\circ F.$), and forms solutions which are colored blue by ferric chloride. The β -acid is difficult to prepare.

Naphthalene-dicarboxylic acids, $C_{10}H_6(CO_2H)_2$.—Of these acids there are three known modifications. Two of them, α and β , are obtained by heating the corresponding dicyanonaphthalenes with strong hydrochloric acid to 200° – $210^\circ C.$ (392° – $410^\circ F.$).— α . Forms long pointed needles, melting with decomposition, above $300^\circ C.$ ($572^\circ F.$); its salts, except those of the alkalis, are but slightly soluble in water. The β -acid is very much like the α -acid, except that it crystallizes in short slender needles.

The third modification, *naphthalic acid*, obtained by oxidation of acenaphthene and acenaphthylene with chromic acid mixture, forms slender needles, and decomposes at 140° – 150° C. (284° – 302° F.), without melting, into water and the anhydride, $C_{10}H_6O_3$, which melts at 260° C. (510° F.). The acid is nearly insoluble in water. Its calcium salt heated with lime yields naphthalene. The *methyl ether*, $C_{10}H_8(CO_2CH_3)_2$, crystallizes in prisms melting at 102° – 103° C. (215.6° – 217.4° F.).

Dinaphthyl, $C_{20}H_{14} = C_{10}H_7 \cdot C_{10}H_7$, is formed by the action of sodium on monobromonaphthalene; by oxidation of naphthalene with MnO_2 and sulphuric acid; and by heating mercuric naphthide with acids (p. 947). Colorless laminae, with a mother-of-pearl lustre; slightly soluble in cold alcohol, easily in ether; melts at 154° C. (309.2° F.), and sublimes without decomposition. By further oxidation with MnO_2 and sulphuric acid it is converted, like naphthalene, into phthalic acid.

Three *isodinaphthyls* are obtained by passing naphthalene-vapour alone, or mixed with antimony trichloride, through a red-hot tube, and may be separated by repeated crystallization from petroleum; melting points, 147° , 147° , and 75° C. (308.6° , 296.6° , 167° F.).

Dinaphthylmethane, $C_{20}H_{16} = C_{10}H_7 \cdot CH_2 \cdot C_{10}H_7$, obtained (like diphenylmethane, p. 935) by the action of sulphuric acid on a mixture of naphthalene and methylal diluted with chloroform, crystallizes in short prisms, melts at 109° C. (228.2° F.), boils at a temperature above 360° C. (680° F.), and may be distilled without decomposition. With picric acid it forms the compound $C_{20}H_{16} \cdot 2C_6H_3(NO_2)_3O$, which crystallizes in reddish-yellow prisms.

Homologues of Naphthalene are obtained by the action of sodium on a mixture of bromonaphthalene and alcoholic bromides dissolved in ether; and these, when passed through red-hot tubes, split up into hydrogen and unsaturated hydrocarbons. *Methyl-naphthalene*, $C_{11}H_8$, is a thick liquid, boiling at 232° C. (449.6° F.), not solidifying at -1° C. (-0.4° F.); *ethyl-naphthalene*, $C_{12}H_{10}$, boils at 251° – 252° C. (483° – 485.6° F.), and does not solidify at -14° C. (6.8° F.).

Acenaphthene, $C_{11}H_8 = C_{10}H_6 \begin{matrix} \diagup CH_2 \\ \diagdown CH_2 \end{matrix}$, is formed by passing ethyl-

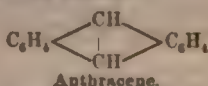
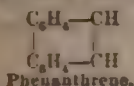
naphthalene through a red-hot tube, and occurs in the portion of coal-tar oil boiling at 250° – 260° C. (482° – 500° F.), from which it may be separated by cooling. It crystallizes from fusion in flat prisms, from alcohol in long needles; melts at 95° C. (203° F.); boils at 277.5° C. (531.5° F.); forms with picric acid the compound $C_{11}H_8 \cdot C_6H_3(NO_2)_3OH$, which crystallizes from alcohol in long needles melting at 161° – 162° C. (321.8° – 323.6° F.). By oxidation with chromic acid mixture, acenaphthene is converted into naphthalic acid (p. 949).

Acenaphthylene, $C_{10}H_6 = C_{10}H_4 \begin{matrix} \diagup CH \\ \diagdown CH \end{matrix}$, is formed by passing the vapor

of acenaphthene over gently heated lead oxide. It dissolves easily in alcohol, crystallizes in yellow tables, sublimes at ordinary temperatures, melts at 92° – 93° C. (197.6° – 199.4° F.), and boils, with partial decomposition, at about 265° – 275° C. (508° – 527° F.). Its picric acid compound forms yellow needles melting at 202° C. (395.6° F.). By chromic acid mixture it is oxidized to naphthalic acid. Its dibromide, $C_{10}H_4Br_2$, melts at 122° C. (251.6° F.).

PHENANTHRENE AND ANTHRACENE GROUP.

The primary compounds of this group are two isomeric solid hydrocarbons, $C_{14}H_{10}$, occurring in the portion of coal-tar which boils between 320° and 360° C. (608° – 680° F.). They are nearly related to benzene, and their modes of formation and decomposition show that their structure may be very probably represented by the following formulae:



Both consist of two benzene residues united by the group C_2H_2 ; but in phenanthrene the two benzene-groups are joined directly, in the same manner as in diphenyl, whereas in anthracene they are united only through the medium of the group $=CH-CH=$.

Phenanthrene. $C_{14}H_{10}$, may be formed by abstraction of hydrogen from dibenzyl, $C_{14}H_{12}$, and stilbene, $C_{14}H_{12}$, when the vapors of these bodies are passed through a red-hot tube; also, together with anthracene and other hydrocarbons, from toluene and xylene, by similar treatment (p. 816).

Phenanthrene is prepared from crude anthracene—the high-boiling portion of coal-tar—by collecting apart the portion which boils between 320° and 350° C. (608° – 662° F.), and boiling the mass with alcohol. The solution on cooling deposits, first anthracene, and then phenanthrene, which may be obtained quite clear by two recrystallizations.

Phenanthrene crystallizes in colorless shining laminae, and exhibits a bluish fluorescence, especially in solution; melts at 100° ; boils at 340° C. (644° F.); dissolves in 50 parts of alcohol at 13° C. (55.4° F.), easily in boiling alcohol, ether, and benzene. It unites with picric acid, a mixture of the saturated alcoholic solutions of the two bodies, depositing the compound $(C_{14}H_{10}.C_6H_3(NO_2)_3O)$, in reddish-yellow needles melting at 143° C. (289.4° F.). By boiling with chromic acid mixture phenanthrene is converted, first into phenanthrene-quinone, and ultimately into diphenic acid (p. 942).

Phenanthrene tetrahydride, $C_{14}H_{14}$, formed by heating phenanthrene to 210° – 240° C. (410° – 464° F.) with hydriodic acid and amorphous phosphorus, is a liquid boiling at 300° – 310° C. (572° – 590° F.).

Phenanthrene dibromide, $C_{14}H_{10}Br_2$, obtained by direct combination in etheral solution, forms prismatic crystals, and is resolved, by heating with water to 100° , into HBr and bromophenanthrene, $C_{14}H_9Br$, which melts at 63° C. (145.4° F.).

Phenanthrene-quinone, $C_{14}H_8O_2 = \begin{array}{c} C_6H_5-CO \\ | \\ C_6H_5-CO \end{array}$, is formed by

heating phenanthrene with chromic acid mixture, or by adding chromic anhydride to a solution of phenanthrene in glacial acetic acid. It crystallizes from alcohol in shining orange-yellow needles, melts at 198° C. (388.4° F.), sublimates without decomposition, dissolves sparingly in hot water and cold alcohol, easily in hot alcohol; dissolves in strong sulphuric acid with dark-green color, and is precipitated therefrom by water. It unites with acid sodium sulphite, forming the compound $C_{14}H_8O_2.SO_3Na + 2H_2O$.

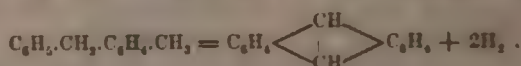
Phenanthrene-quinone is oxidized by chromic acid mixture to diphenic

acid, and reduced by zinc-dust to phenanthrene; when ignited with soda-lime it yields diphenyl.

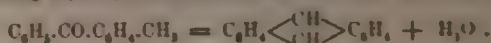
Phenanthrene-hydroquinone, or *Dioxyphenanthrene*, $C_{14}H_8(OH)_2$, formed by the action of sulphurous acid on phenanthrene-quinone, crystallizes in colorless needles, which, when exposed to the air, turn brown, and are reoxidized to the quinone. Its diacetyl-compound crystallizes in tables melting at 202°C . (395.6°F .).

Anthracene, $C_{14}H_{10}$.—This hydrocarbon may be formed artificially.

1. By passing benzyl-toluene through a red-hot tube or over heated lead oxide:



2. By heating liquid phenyl-tolyl ketone (p. 341) with zinc-dust:



3. Together with dibenzyl, by heating benzyl chloride with water to 190°C . (374°F .):



Anthracene is prepared from the high-boiling portions of coal-tar by repeated distillation, pressure, and recrystallization from benzene. To obtain it quite pure and colorless, it must be sublimed at as low a temperature as possible—best by heating it till it begins to boil, and then blowing a strong current of air over it from a pair of bellows. Or its solution in hot benzene may be bleached by exposure to sunshine.

Anthracene crystallizes in colorless monoclinic tables, exhibiting a fine blue fluorescence. It dissolves sparingly in alcohol and ether, easily in hot benzene; melts at 213°C . (415.4°F .), and distils at a temperature a little above 360°C . (680°F .). Its solution in benzene yields with peracetic acid the compound $C_{14}H_{10}.2(C_2H_5(NO_2))_2O$, which crystallizes in red needles.

A cold saturated solution of anthracene in benzene exposed to sunshine deposits tabular crystals of an isomeric modification, $C_{14}H_{10}$, called *par-anthracene*. It is nearly insoluble in benzene, is not attacked by nitric acid or bromine, melts at 244°C . (471.2°F .), and is at the same time converted into ordinary anthracene.

Anthracene dihydride, $C_{14}H_{12}$, formed by heating anthracene or anthraquinone with hydriodic acid and phosphorus, or by the action of sodium-amalgam on its alcoholic solution, crystallizes in monoclinic tables easily soluble in alcohol, melting at 106°C . (222.8°F .), distilling at 260°C . (581°F .). On passing its vapor through a red-hot tube, it is resolved into anthracene and hydrogen. The *hexahydride*, $C_{14}H_{16}$, is formed by prolonged heating of anthracene or the dihydride with HI and phosphorus to 200 – 220°C . (392 – 422°F .), crystallizes in laminae, melts at 63°C . (145.4°F .), boils at 290°C . (554°F .). It is very soluble in alcohol, ether, and benzene, and is resolved at a red heat into anthracene and hydrogen.

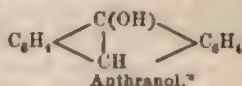
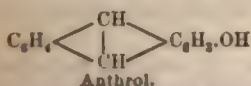
Anthracene dichloride, $C_{14}H_{10}Cl_2$, formed by passing chlorine gas over anthracene, crystallizes in needles, and is converted by alcoholic potash into $C_{14}H_8Cl_2$. By heating anthracene in chlorine, dichloro-anthracene, $C_{14}H_8Cl_2$, is formed, which crystallizes in yellow laminae, melts at 209°C . (408.2°F .), and yields solutions having a splendid blue fluorescence.

Dibromanthracene, $C_{14}H_8Br_2$, is formed as the sole product of the action of bromine on a solution of anthracene on carbon sulphide. It crystallizes in golden-yellow needles, melting at $221^\circ C.$ ($429.8^\circ F.$), and is reconverted into anthracene by heating with alcoholic potash. Dibromanthracene tetrabromide, $C_{14}H_8Br_2 \cdot Br_2$, is formed by passing bromine vapor over finely divided anthracene or dibromanthracene. Hard, thick, colorless tables, melting with decomposition at $170^\circ\text{--}180^\circ C.$ ($338^\circ\text{--}356^\circ F.$).

Another modification of dibromanthracene is formed by heating dibromanthracene with HI and phosphorus to $150^\circ C.$ ($302^\circ F.$) for eight hours. Golden-yellow tables, melting at $190^\circ\text{--}192^\circ C.$ ($374^\circ\text{--}377.6^\circ F.$), more soluble in alcohol and benzene than the preceding modification.

Anthracene-sulphonic acids, *mono-* and *di-*, are formed by heating anthracene with strong sulphuric acid, the former at 100° , the latter at $150^\circ C.$ ($302^\circ F.$). The monosulphonic acid is produced in two isomeric modifications (*a* and *b*), which may be separated by means of their lead-salts. That of the *a*-acid (the chief product) crystallizes in light yellow laminae $(C_{14}H_9SO_3)_2Pb + 4H_2O$, and is much more soluble than that of the *b*-acid, which crystallizes in prisms containing $7H_2O$.

Anthraphenols, $C_{14}H_{10}O = C_{14}H_9(OH)$.—Of these bodies there are two metameric modifications, viz.:



Anthrol is formed in two isomeric modifications by fusing the alkalis of the two isomeric anthracene-monosulphonic acids with potash or soda.

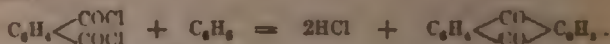
a. Light yellow needles or laminae having a strong lustre, decomposing at $250^\circ C.$ ($482^\circ F.$) without previous fusing; insoluble in water, easily soluble in alcohol, ether, benzene, and alkalies. The alkaline solution absorbs oxygen from the air, and turns brown.

b. Yellowish prisms, somewhat less soluble in alcohol and ether than *a*, which it otherwise resembles in every respect.

Anthranol is formed by heating anthraquinone (20 parts) with hydriodic acid of 1.7 sp. gr. (80 parts) and phosphorus (4 parts) in a vessel with reversed condenser. It crystallizes in yellowish needles, melts at $163^\circ\text{--}170^\circ C.$ ($325.4^\circ\text{--}338^\circ F.$), is nearly insoluble in cold, more soluble in hot alkalies. The solution absorbs oxygen from the air, and then deposits anthraquinone on boiling. Anthranol is also converted into anthraquinone by oxidation with nitric or chromic acid, and into anthracene by heating with zinc-dust. With acetic anhydride, it forms an acetic ether, $C_{14}H_9O.C_2H_5O$, which crystallizes in light yellow needles melting at $126^\circ\text{--}131^\circ C.$ ($258.8^\circ\text{--}267.8^\circ F.$).

Anthraquinone, $C_{14}H_8O_2 = C_6H_5 \begin{array}{c} \diagup CO \\ | \\ CO \diagdown \end{array} C_6H_5$.—This compound, which may be regarded as a double ketone, and differs from the quinones of the benzene series in not having its two oxygen-atoms directly combined, is formed by oxidation of anthracene, anthracene-hydride, dichlor- or dibromanthracene, with nitric or chromic acid; also when liquid phenyl-tolyl ketone (p. 941), $C_6H_5.CO.C_6H_4.CH_3$, is passed over heated lead oxide, or heated with MnO_2 and sulphuric acid, or with chromic acid mixture; in small quantity also (together with benzophenone, p. 941) by distillation

of calcium benzoate;—and by heating phthalic chloride and benzene with zinc-dust:



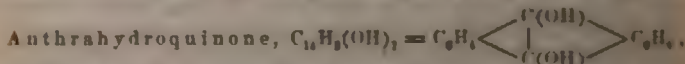
It is most easily prepared by adding finely pounded potassium dichromate, or a solution of chromic acid in glacial acetic acid, to a hot solution of anthracene in glacial acetic acid.

Anthraquinone sublimes in shining yellow needles, melts at $273^{\circ}C.$ ($523.4^{\circ}F.$), dissolves in hot benzene and in nitric acid. It is a very stable compound, not easily altered by oxidizing agents, and not reduced by sulphurous acid, like the quinones of the benzene series. Heated with hydriodic acid to $150^{\circ}C.$ ($302^{\circ}F.$), or with zinc-dust, it is converted into anthracene. By fusion with potash at $250^{\circ}C.$ ($482^{\circ}F.$), it yields 2 molecules of benzoic acid. Heated with PCl_5 to $190-200^{\circ}C.$ ($374-392^{\circ}F.$) it yields a mixture of di- and tetra-chloranthracene; and when heated with fuming sulphuric acid, it yields sulpho-acids, together with phthalic anhydride.

Dibromanthraquinone, $C_{14}H_6Br_2O_2$, is formed by heating anthraquinone with bromine to 100° , or by oxidizing tetrabromanthracene with nitric acid; dichloranthraquinone is formed by a similar method. Both sublime in yellow needles, and are converted into alizarin by heating with potash-lye to $150^{\circ}C.$ ($302^{\circ}F.$).

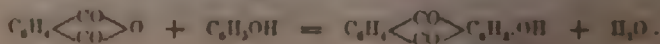
Dinitro-anthraquinone, $C_{14}H_6(NO_2)_2O_2$, obtained by boiling anthracene with dilute nitric acid, forms yellow needles melting at 246° , and, like picric acid, forms crystalline compounds with many hydrocarbons. An isomeric compound, obtained by the action of a mixture of nitric and sulphuric acids on anthraquinone, forms small light yellow monoclinic prisms, cakes together at $252^{\circ}C.$ ($485.6^{\circ}F.$), and sublimes at a higher temperature in small needles, with partial decomposition.

Anthraquinone-sulphonic acid, $C_{14}H_6O_2 \cdot SO_3H$, and the disulphonic acid, $C_{14}H_6O_2(SO_3H)_2$, are formed, together with phthalic anhydride, by heating anthraquinone with strong sulphuric acid to $250-260^{\circ}C.$ ($482-500^{\circ}F.$). The disulphonic acid is formed synthetically by heating orthobenzoyl-benzoic acid, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot CO_2H$ (p. 945), with fuming sulphuric acid. It forms yellow crystals easily soluble in water.



produced by heating anthraquinone with zinc-dust and potash-lye, forms yellow flakes, which, especially when moist, are quickly reconverted into anthraquinone by exposure to the air.

Oxyanthraquinone, $C_{14}H_8O_2 = C_6H_5 \begin{array}{c} \diagup CO \\ | \\ \diagdown CO \end{array} C_6H_4(OH)$.—This compound is produced, together with alizarin, by fusing monobromanthraquinone or anthraquinone-sulphonic acid with potassium hydroxide, by boiling the product with water and calcium or barium carbonate, the alizarin is precipitated, and the oxyanthraquinone dissolved. Oxyanthraquinone is formed synthetically, together with its isomeric, *oxybenzanthraquinone*, by heating phthalic anhydride and phenol with strong sulphuric acid:

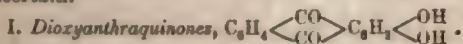


The two isomerides may be separated by ammonia in which oxyanthraquinone is soluble, erythroxyanthraquinone insoluble.

Oxyanthraquinone is equally soluble in hot and in cold alcohol, crystallizes in sulphur-yellow needles, melts at 268° – 271° C. (514.4° – 519.8° F.), and sublimes with some difficulty in laminae. It dissolves readily in ammonia, baryta-water, and lime-water, and decomposes barium carbonate when boiled with it in water.

Erythroxyanthraquinone is more soluble in hot than in cold alcohol, crystallizes in orange-yellow needles, melts at 173° – 180° C. (343.4° – 356° F.), and sublimes at 150° C. (302° F.). It is nearly insoluble in dilute ammonia, forms dark-red lakes with baryta- and lime-water, and (like alizarin) does not decompose carbonate of barium. Both oxyanthraquinones are converted by fusion with potash into alizarin.

Dioxyanthraquinones, $C_{14}H_6O_4 = C_{14}H_4(OH)_2O_2$.—This formula includes eight known compounds, in three of which the two hydroxyl-groups are situated in the same benzene-nucleus, while four others have one hydroxyl in each benzene-nucleus, and in the eighth, the position of these groups is uncertain.



1. **ALIZARIN**.—This compound, in which the two hydroxyls are supposed to stand to one another in the para-position, is the red coloring matter of madder root (*Rubia tinctorum*). Fresh madder roots contain a glucoside, called ruberythric acid, which, when the roots are steeped in water, is resolved, under the influence of a peculiar ferment also contained in them, into alizarin and glucose:



In old roots this change has already taken place to a considerable extent, so that they contain free alizarin. This spontaneous change was the basis of the older method of obtaining alizarin, and of the use of madder in dyeing. Various methods of accelerating the decomposition have been invented, in particular the treatment of the pulverized root, previously exhausted with water, with strong sulphuric acid, which decomposes the ruberythric acid in the manner above explained, but does not alter the resulting alizarin. The product thus obtained is called garancin.

At present, however, almost all the alizarin used in dyeing is obtained by artificial processes from anthracene. It may be obtained by the action of melting potash on various derivatives of anthracene, viz., dibrom- and dichlor-anthraquinone, the two monoxyanthraquinones, and anthraquinone-disulphonic acid. Graebe and Liebermann, in 1868, first prepared it from dibromanthraquinone, and Perkin soon afterwards showed that it might be obtained much more economically from anthraquinone-disulphonic acid. This last method is now carried out on a very large scale. The mass obtained by fusion with potash is dissolved in water, and the alizarin, precipitated by hydrochloric acid, is purified by crystallization and sublimation.

Alizarin crystallizes from alcohol in reddish-yellow prisms or needles containing 3 mol. H_2O , which it gives off at 100° . It melts at 275° C. (527° F.) (Liebermann & Troschke); at 280° – 290° C. (552.2° – 554° F.) (Claus & Willgerodt),* and sublimes in orange-colored needles; dissolves sparingly in hot water, easily in alcohol and ether; also in strong sulphuric acid, forming a dark-red solution, from which it is precipitated by water in its original state.

* Deutsch. Ch. Ges. Ber. 1873, pp. 361, 381.

Alizarin has the structure of a diatomic phenol, and reacts like a weak acid. It dissolves in alkalis, forming purple solutions, from which sodium and barium salts throw down the corresponding salts as purple precipitates (distinction from monoxanthraquinone).

Aluminium- and tin-salts form red precipitates (madder-lakes), ferric salts, a black-violet precipitate. The use of alizarin in dyeing and calico-printing is founded on this property of forming insoluble colored compounds with metallic salts.

Alizarin is converted by heating with zinc-dust into anthracene, and by oxidation with nitric acid into phthalic acid.

Alizarin boiled with acetic anhydride yields first *monacetyl-alizarin*, $C_{14}H_6(OH)(OC_2H_3O)_O$, and after prolonged boiling, *diacetyl-alizarin*, $C_{14}H_4(OC_2H_3O)_2O$.

Alizarinumide, $C_6H_4.C_2O_2.C_6H_2(NH_2)OH$, formed by heating alizarin with aqueous ammonia to 150° – 200° C. (302° – 392° F.), crystallizes in brown needles, melting at 250° – 260° C. (482° – 500° F.).

2. **QUINIZARIN** is formed by heating phthalic anhydride and hydroquinone, or parachlorophenol, with sulphuric acid. It crystallizes from ether in yellow needles melting at 194° C. (381.2° F.); dissolves in alkalis with blue-violet color; forms blue-violet precipitates with baryta and magnesia, red with alumina; and is reduced to anthracene by heating with zinc-dust.

3. **PURPURIXANTHIN** (or *Xanthropurpurin*) occurs in small quantity in madder, and is formed from purpurin by reduction with stannous chloride in alkaline solution. Yellowish-red needles, m. p. 262° – 266° C. (503.6° – 505.4° F.); dissolving with red color in alkalis and baryta-water. In alkaline solution it absorbs oxygen from the air.

Purpuroxanthic Acid, $C_{15}H_8O_6 = C_{14}H_7O_5.CO_2H$, is a constituent of commercial purpurin, from which it may be extracted by means of boiling alum-liquor. It is more soluble in boiling water than most madder colors; crystallizes from hot alcohol in yellow needles; melts at 231° C. (447° F.), and splits up at 232° – 233° C. (449.6° – 451.4° F.) into CO_2 and purpuroxanthin. It dissolves in a boiling solution of ferric chloride with deep reddish-brown color, and is reprecipitated by hydrochloric acid in yellow flocks.

Purpuroxanthic acid is most probably identical with *Munfiatis*, a coloring matter extracted some years ago by Dr. Stenhouse from *Mucijet* or East Indian madder, this substance being also resolved by heat into CO_2 and purpuroxanthin (Schunk and Roemer, *Chem. Soc. Journal*, 1877, 1. 606).

II. Dioryanthraquinones, $C_6H_2(OH) \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C_6H_2(OH) \cdot$

4. **ANTHRAPLAVONE**.—Formed from oxybenzoic acid, $C_6H_4(OH).CO.OH$, in small quantity by dry distillation, in larger quantity by heating with sulphuric acid to 180° – 200° C. (356° – 392° F.). Crystallizes in small yellow needles; sublimes above 300° C. (572° F.) with partial decomposition, and without previous fusion; nearly insoluble in boiling water, slightly soluble in ether, more easily in alcohol; dissolves with brown color in alkalis; converted into alizarin by heating with zinc-dust, into oxybenzoic acid by fusion with potash.

5. **ANTHRAPLAVIC ACID**.—Formed, together with iso-anthravlavic acid, from two different anthraquinone-disulphonic acids, in the preparation of alizarin on the large scale. It is therefore a constituent of crude commercial alizarin, and may be extracted therefrom by lime-water (the alizarin

remaining undissolved), the red solution being precipitated with hydrochloric acid, and the precipitate treated with cold baryta-water, which dissolves iso-anthrallavic acid, and leaves the anthrallavic acid undissolved.

Anthrallavic acid crystallizes from alcohol in anhydrous yellow silky needles; melts above 330° C. (626° F.); dissolves in alkalis, with yellowish-red color; forms with acetic anhydride a diacetyl-compound, $C_{14}H_6(OC_2H_3O)_2$, melting at 227° C. (440.6° F.).

8. ISO-ANTHRALLAVIC ACID, prepared as above, crystallizes from aqueous alcohol in long yellow needles with 1 mol. H_2O , which is given off at 150° C. (302° F.); the anhydrous compound melts above 330° C. (626° F.). Dissolves in alkalis with deep-red color. The diacetyl-compound forms small pale-yellow crystals melting at 195° C. (383° F.).

7. CHRYSAZIN, prepared by heating with alcohol the diazo-compound formed by the action of nitrous acid on sulphate of hydrochrysaumide (*infra*), crystallizes in golden-yellow laminae or red-brown highly lustrous needles; melts at 191° C. (375.8° F.); dissolves in alkalis with yellowish-red color; forms insoluble red compounds with lime- and baryta-water; is reduced to anthracene by heating with zinc-dust. The diacetyl-compound forms yellowish laminae melting at 226° – 230° C. (438.8° – 446° F.).

Tetranitrochryszazin, or Chrysaumic acid, $C_{14}H_2(NO_2)_4(OH)_2O_2$, formed by heating aloes, or chryszazin, with strong nitric acid, crystallizes in golden-yellow laminae sparingly soluble in water, and reacts like a strong bibasic acid. By the action of reducing agents it is converted into tetramido-chryszazin or chrysaumide, $C_{14}H_2(NH_2)_4(OH)_2O_2$, which crystallizes in indigo-blue needles, having a splendid coppery lustre.

8. FRANGULIC ACID, $C_{14}H_8O_4 + 1\frac{1}{2}H_2O$, a dioxyanthraquinone in which the relative positions of the two OH groups are not known, is formed by the action of dilute acids on frangulin, $C_{20}H_{26}O_{10}$, a glucoside contained in the bark of *Rhamnus frangula*. It crystallizes in orange-yellow needles or plates containing $1\frac{1}{2}$ mol. H_2O , gives off its water at 180° C. (356° F.), and melts at 252° – 254° C. (485.6° – 489.2° F.). Reduced by zinc-dust to anthracene.

Trioxanthraquinones, $C_{14}H_6O_6 = C_{14}H_2(OH)_2O_2$.—Of these compounds there are four known modifications:

1. PURPURIN, $C_6H_2\langle\begin{smallmatrix} CO \\ CO \end{smallmatrix}\rangle C_6H(OH)_2$, occurs in old madder-root, together with alizarin, and may be separated by means of boiling alum solution, in which the alizarin is insoluble. It may be formed artificially from alizarin or chryszazin by oxidation with MnO_2 and sulphuric acid at 140° – 160° C. (284° – 320° F.), and from purpuroxanthin by merely heating the alkaline solution in an open vessel. It crystallizes in reddish-yellow prisms, easily fusible, and subliming with partial decomposition; somewhat more soluble in water than alizarin; dissolves with red color in alcohol, ether, and alkalis; forms purple-red precipitates with lime- and baryta-water; is reduced to anthracene by heating with zinc-dust. With acetic anhydride it forms a triacetyl-compound, $C_{14}H_2(OC_2H_3O)_3$, which crystallizes in yellowish needles melting at 190° – 193° C. (374° – 379.4° F.).

Purpurinamide, $C_{14}H_2(NH_2)(OH)_2O_2$, obtained by heating purpurin with

aqueous ammonia, forms brownish-green metallicallly lustrous needles. Treated in hot alcoholic solution with nitrous acid, it is converted into purpuroxanthin.

2. **ANTHRAPURPURIN**, $C_6H_5OH.C_2O_2.C_6H_2(OH)_2$, produced by fusing potassium anthraquinone-disulphonate or isoanthraflavic acid with potash, forms orange-colored needles, melting above $330^\circ C.$ ($626^\circ F.$), sublimable with partial decomposition. Dissolves in alkalis with fine violet color, and, like alizarin, produces red colors with alumina-mordants, purple and black with iron-mordants; but the reds are purer than those of alizarin, the purples bluer, and the blacks more intense. Its triacetyl-compound forms light-yellow scales melting at $220^\circ-223^\circ C.$ ($428^\circ-431.6^\circ F.$).

3. **FLAVOPURPURIN**, $C_6H_5OH.C_2O_2.C_6H_2(OH)_2$, formed from anthraflavic acid by fusion with potash, crystallizes from alcohol in golden-yellow needles, melts above $330^\circ C.$ ($626^\circ F.$), sublimes in long needles, like alizarin. Dissolves easily in alcohol, with purple color in alkalis.

4. **OXYCHRYSAZIN**, $C_6H_5(OH).C_2O_2.C_6H_2(OH)_2$, produced by the action of melting potash on chrysazin, is precipitated from its bluish-violet solution in alkalis by acids in brown flocks, and crystallizes from alcohol. Its triacetyl-compound forms light-yellow needles melting at $192^\circ-193^\circ C.$ ($377.6^\circ-379.4^\circ F.$).

5. **Pseudopurpurin**.—This is a constituent of crude purpurin, hitherto regarded as a dioxyalizarin or tetraoxyanthraquinone, $C_{14}H_6O_8$, but lately shown by Rosenstiehl (*Comptes rendus*, lxxxiv. 561) to consist of purpurin-carbonic acid, $C_{12}H_6O_7 = C_{14}H_6O_5.CO_2H$, inasmuch as it is resolved by heat into CO_2 and purpurin. It is also readily converted into purpurin by alkalis, even at ordinary temperatures.

Tetraoxyanthraquinone, $C_{14}H_4(OH)_4O_8$, is known in two modifications:—

1. **ANTHRACHRYSONE**, $C_6H_2(OH)_2.C_2O_2.C_6H_2(OH)_2$, is formed, like anthraflavone, from dioxybenzoic acid, $C_6H_2(OH)_2.CO.OH$, by dry-distillation, or by heating to $140^\circ C.$ ($284^\circ F.$) with strong sulphuric acid. It is insoluble in water, crystallizes from glacial acetic acid or from alcohol in yellowish-red needles, melting at $320^\circ C.$ ($608^\circ F.$); yields anthracene when heated with zinc-dust.

2. **RUFIOFIN**, $C_{14}H_4(OH)_4O_8$, obtained by heating opianic acid (p. 923) with sulphuric acid, forms yellowish-red needles or crusts, dissolving in alkalis with violet-red color; yields anthracene by reduction with zinc-dust.

A third modification is perhaps *Pseudopurpurin*, which is contained in madder-root. It is very much like purpurin, is converted into that substance by boiling with water or alcohol, and is said to be converted by reducing agents into purpuroxanthin.

Rufigallic acid, $C_{14}H_6O_8$, obtained by heating gallic or digallic acid with strong sulphuric acid, is a hexoxyanthraquinone, $C_6H(OH)_3.C_2O_2.C_6H(OH)_3$. It forms small, shining, brown-red crystals, containing $2H_2O$, which it gives off at $120^\circ C.$ ($248^\circ F.$), and sublimes at a higher temperature in cinnabar-red prisms; dissolves sparingly in hot water, alcohol, and ether, with brown color in alkalis; precipitated with indigo-blue color by baryta-water. Yields anthracene by reduction with zinc-dust.

Methyl-anthracene, $C_{15}H_{12} = C_{14}H_9.CH_3$, is formed by passing the vapor of ditolyl-methane or ditolyl-ethane (p. 936) through a red-hot tube, and by heating chrysophanic acid, emodin or eloin, with zinc-dust. Colorless shining laminae, melting at $200^{\circ}C.$ ($392^{\circ}F.$); slightly soluble in alcohol, ether, and glacial acetic acid; easily in chloroform, CS_2 , and benzene. Forms with *picric acid* a compound which crystallizes in long dark-red needles, and is decomposed by water and alcohol.

Methylantraquinone, $C_{15}H_{10}O_2 = C_6H_5.C_2O_2.C_6H_5(CH_3)$, obtained by oxidizing methylantracene in alcoholic solution with nitric acid, forms small yellow needles, melting at $162^{\circ}C.$ ($323.6^{\circ}F.$).

Dioxymethylantraquinone, $C_{15}H_{10}O_4 = C_{14}H_9.CH_3(OH)_2.O_2$, is known in two modifications:

1. **Methylalizarin** is formed by the action of melting potash on the potassium salt of methylantraquinone-sulphonic acid. It closely resembles alizarin; sublimes above 200° in tufts of small red crystals; melts at $250^{\circ}C.$ ($482^{\circ}F.$); dissolves in alkalis with blue-violet color.

2. **Chrysophanic acid** (*Parietic acid*, *Rheic acid*) occurs in the lichen *Parmelia parietina*, in senna leaves, and in rhubarb root, and may be extracted therefrom by ether or alkalis. It crystallizes in golden-yellow needles or prisms, melts at $162^{\circ}C.$ ($323.6^{\circ}F.$), and sublimes partly without decomposition; dissolves in alkalis with red color; is reduced by zinc-dust to methyl-anthracene.

Trioxymethylantraquinone or **Emodin**, $C_{15}H_{10}O_5 = C_{14}H_9(CH_3)(OH)_3.O_2$, occurs in the bark of *Rhamnus frangula*, and in small quantity, together with chrysophanic acid, in rhubarb root, and is separated by solution of sodium carbonate, which dissolves the emodin, leaving the chrysophanic acid. Long, brittle orange-red, monoclinic prisms, melting at $245^{\circ}C.$ ($473^{\circ}F.$); converted into methyl-anthracene by heating with zinc-dust.

Anthracene carbonic Acid, $C_{14}H_9.CO_2H$, is obtained by heating anthracene with carbonyl chloride to $200^{\circ}C.$ ($392^{\circ}F.$) in sealed tubes, dissolving the product in sodium carbonate, and precipitating with hydrochloric acid. Long, silky, light yellow needles, melting with decomposition at $206^{\circ}C.$ ($402.8^{\circ}F.$); slightly soluble in hot water, easily in alcohol. Oxidized by chromic acid to anthraquinone; resolved by heat into CO_2 and anthracene. An isomeric acid, obtained by saponification of the cyanide produced by heating potassium anthracene-sulphonate with potassium ferrocyanide, melts above $220^{\circ}C.$ ($428^{\circ}F.$), and sublimes without decomposition in orange-yellow needles.

Hydrocarbons of Higher Boiling Point.

Pyrene, $C_{16}H_{10}$, and **Chrysene**, $C_{18}H_{12}$, are contained in the portion of coal-tar boiling above $360^{\circ}C.$ ($680^{\circ}F.$) (b. p. of anthracene), and may be separated by heating the solid mass with carbon sulphide, which dissolves pyrene, together with other hydrocarbons, while the chrysene remains behind.

Pyrene may be obtained pure by distilling off the carbon sulphide, dissolving the residue in alcohol, and adding an alcoholic solution of picric acid. Red crystals then separate, consisting of a compound of pyrene and picric acid, which, after purification by repeated crystallization from alcohol, may be decomposed by ammonia. Pyrene crystallizes in plates, melts at $142^{\circ}C.$ ($287.6^{\circ}F.$), and distils at a higher temperature; dissolves

sparingly in cold, more readily in hot alcohol; very easily in benzene, ether, and carbon sulphide. Its picric acid compound, $C_{16}H_{10} \cdot C_6H_3(NO_2)_3O$, crystallizes in red needles. Heated with hydriodic acid to $200^\circ C.$ ($392^\circ F.$), it is converted into a hexahydride, $C_{16}H_{10} \cdot H_6$, melting at $127^\circ C.$ ($260.6^\circ F.$). Heated with chromic acid mixture, it yields pyrene quinone, $C_{16}H_8O_2$, which sublims in red needles.

Chrysene, $C_{18}H_{12}$, the portion of the high-boiling coal-tar hydrocarbons which is insoluble in carbon sulphide, may be purified by repeated crystallization from benzene. It is thus obtained in bright yellow glistening scales, which cannot be decolorized by recrystallization, but may be obtained quite colorless by heating with hydriodic acid and amorphous phosphorus to $240^\circ C.$ ($464^\circ F.$), or by boiling with alcohol and a small quantity of nitric acid. It dissolves very sparingly in alcohol, ether, and carbon sulphide, more freely in benzene; sublims in dazzling white laminae, which exhibit a fine blue fluorescence, and melt at $250^\circ C.$ ($482^\circ F.$). Its picric acid compound, $C_{18}H_{12} \cdot C_6H_3(NO_2)_3O$, crystallizes in brown needles. By oxidation with chromic anhydride dissolved in glacial acetic acid, it yields chrysene-quinone, $C_{18}H_{10}O_2$, which crystallizes in red needles, melts at $235^\circ C.$ ($455^\circ F.$), dissolves with fine blue color in strong sulphuric acid, and is precipitated from the solution by water in its original state. Chrysene-quinone unites with acid sodium sulphite, and is reduced by sulphurous acid to chrysohydroquinone, $C_{18}H_{10}(OH)_2$. By distillation with soda-lime it yields the hydrocarbon $C_{18}H_{12}$ (m. p. 104° – $105^\circ C.$, 219.2° – $221^\circ F.$), just as phenanthrene-quinone yields diphenyl (p. 561).

Retene, $C_{19}H_{14}$, occurs in thin unctuous scales on fossil pine-stems, in beds of peat and lignite, in Denmark and other localities. It is produced in the dry distillation of very resinous fir and pine wood, passing over together with the heavy tar-oil, and separating in scales like paraffin; also, together with other hydrocarbons, by passing acetylene through red-hot tubes. It crystallizes in colorless laminae, slightly soluble in alcohol, easily in ether; melts at $99^\circ C.$ ($210.2^\circ F.$); forms with picric acid the compound $C_{19}H_{14} \cdot C_6H_3(NO_2)_3O$, which crystallizes in orange-yellow needles. It is converted by sulphuric acid into a disulphonic acid, and by chromic acid mixture into dioxyretistene, $C_{19}H_{14}O_2$ (m. p. 194° – $195^\circ C.$, 381.2° – $383^\circ F.$), and phthalic acid. Dioxyretistene, heated with zinc-dust, is converted into retistene, $C_{19}H_{14}$, which crystallizes from alcohol in white laminae, and forms a crystalline compound with picric acid.

Similar but less known hydrocarbons are *Fichtelite*, found on old pine-stems; *Idrialin*, in quicksilver ore from Idria; and *Scheererite*, in beds of lignite.

TERPENES and CAMPHORS.

The terpenes, $C_{10}H_{16}$, are volatile oils existing in plants, chiefly of the coniferous and aurantiaceous orders. They have not yet been formed by any artificial process, but their relation to the aromatic group is shown by their conversion into terephthalic acid by oxidation with nitric acid, and by the formation of cymene from turpentine oil (p. 819).

Turpentine oil, the most important member of the group, is contained in the wood, bark, leaves, and other parts of pines, firs, and other coniferous trees, and is usually prepared by distilling crude turpentine,

the oleo-resinous juice which exudes from incisions in the bark of the trees, either alone or with water. It was formerly supposed that all the volatile oils thus obtained, and having the composition $C_{10}H_{16}$, were identical in chemical and physical properties; but recent investigations, especially those of Berthelot, have shown that the turpentine oils obtained from different sources exhibit considerable diversities in their physical, and more especially in their optical properties; further, that most kinds of turpentine oil are mixtures of two or more isomeric or polymeric hydrocarbons, differing in physical and sometimes also in chemical properties. These modifications are often produced by the action of heat and of chemical reagents during the purification of the oil.

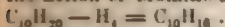
The several varieties of turpentine oil, when purified by repeated rectification with water, are colorless mobile liquids, having a peculiar aromatic but disagreeable odor. They are insoluble in water, slightly soluble in aqueous alcohol, miscible in all proportions with absolute alcohol, ether, and carbon disulphide. They dissolve iodine, sulphur, phosphorus, and many organic substances which are insoluble in water, such as fixed oils and resins, and are therefore used for making varnishes.

The principal varieties are, French turpentine oil, obtained from the French or Bordeaux turpentine of *Pinus maritima*, and English turpentine oil, from the turpentine collected, in Carolina and other Southern States of the American Union, from *Pinus australis* and *Pinus Tada*.

French turpentine oil, when purified by neutralizing it with an alkaline carbonate, and then distilling it, first over the water-bath, and then in a vacuum (by which treatment all transformation of the product by heat or by reagents is avoided), consists mainly of a hydrocarbon, $C_{10}H_{16}$, called terebenthene. It has a specific gravity of 0.864, boils at $161^{\circ}C.$ ($321.8^{\circ}F.$), and turns the plane of polarization of a ray of light to the l.-r. English turpentine oil, treated in a similar manner, yields, as its chief constituent, a liquid called australene, or austraterebenthene, having the same specific gravity and boiling point as terebenthene, but turning the plane of polarization to the right.

When pure turpentine oil (terebenthene or australene) is heated to $200^{\circ}\text{--}250^{\circ}C.$ ($392^{\circ}\text{--}482^{\circ}F.$), it undergoes a molecular transformation, and may then be separated by distillation into two oils, one called astrapylene, isomeric with the original oil, and boiling at $176^{\circ}\text{--}178^{\circ}C.$ ($348.8^{\circ}\text{--}352.4^{\circ}F.$); the other, called metaterebenthene, polymeric with the original oil, having the formula $C_{20}H_{32}$, and boiling at a temperature above $360^{\circ}C.$ ($680^{\circ}F.$). Both are levorotatory, the latter exhibiting the greater amount of rotatory power.

Turpentine oil is converted, by repeated distillation with a small quantity of strong sulphuric acid, into two inactive modifications, terebene, $C_{10}H_{16}$, boiling at $160^{\circ}C.$ ($320^{\circ}F.$), and colophene, $C_{20}H_{32}$, boiling at a very high temperature. A body of the same percentage composition, and closely resembling terebene in its physical properties, is obtained by the action of bromine and alcoholic potash on diamylene (p. 508):



Turpentine oil exposed to the air absorbs oxygen, and acquires powerful oxidizing properties, formerly supposed to be due to the conversion of the oxygen into ozone; but according to recent experiments by Kingzett,* it appears highly probable that the oxidizing compound is an organic peroxide, $C_{10}H_{14}O_4$, which when heated with water is resolved into hydrogen dioxide and camphoric acid: $C_{10}H_{14}O_4 + 2H_2O = H_2O_2 + C_{10}H_{16}O_4$.

Nitric acid and other powerful oxidizing agents convert turpentine oil

* Chem. Soc. Journ. 1874, 511; 1875, 214.

into a number of acid products of complex constitution. Strong nitric acid acts very violently on turpentine oil, sometimes setting it on fire.

Chlorine is absorbed by turpentine oil, with evolution of heat, sometimes sufficient to produce inflammation. When paper soaked in rectified turpentine oil is introduced into a vessel filled with chlorine, the turpentine takes fire, and a quantity of black smoke is produced, together with white fumes of hydrochloric acid. Bromine acts in a similar manner. Iodine is dissolved by turpentine oil, forming at first a green solution, which afterwards becomes hot, and gives off hydriodic acid. When a considerable quantity of iodine is suddenly brought in contact with turpentine oil, explosion frequently ensues. Turpentine oil distilled with chloride of lime and water, yields chloroform.

Nitrosoterpene, $C_{10}H_{15}(NO)$.—When gaseous nitrosyl chloride, $NOCl$ (obtained by passing the gases evolved from heated nitrohydrochloric acid into strong sulphuric acid, and heating the resulting solution with sodium chloride), is passed into oil of turpentine cooled by ice and salt, a white crystalline substance is precipitated, having the composition $C_{10}H_{15}.NOCl$, and this when heated with alcoholic soda gives up HCl and is converted into nitrosoterpene. On acidulating with acetic acid, evaporating to dryness, washing the residue with water, and crystallizing it from alcohol, the nitrosoterpene is obtained in monoclinic crystals melting at 129° – 130° C. (264.2° – 266° F.), and subliming at a somewhat higher temperature. It burns easily, but is not explosive. Sodium-amalgam reduces it to a hydrocarbon.

Compounds of Turpentine oil.—Turpentine oil forms several compounds with hydrochloric acid. The gaseous acid converts it into the monohydrochloride, $C_{10}H_{15}.HCl$. On the other hand, when the oil is subjected for several weeks to the action of the strong aqueous acid, crystals of a dihydrochloride, $C_{10}H_{15}.2HCl$, are obtained. This latter compound is also formed by the action of hydrochloric acid gas on *terpenol*, hence it is called *citrene dihydrochloride*. By the action of hydrochloric acid on *terebene*, the compound $C_{20}H_{33}.HCl$ is formed, called *diterebene hydrochloride*. Lastly, when a current of hydrochloric acid gas is passed through a solution of turpentine oil in acetic acid, the compound $C_{20}H_{33}.3HCl$ is produced, called *dipyrrolene hydrochloride*.

Hydrobromic and hydriodic acids form, with oil of turpentine, compounds analogous in composition to the hydrochlorides; the dihydriodide, however, has not been obtained from turpentine oil itself.

Whatever method may be adopted for preparing the hydrochlorides, hydrobromides, or the monohydriodide of turpentine oil, there are always two isomeric modifications obtained—one liquid, the other solid and crystalline. The crystallized monohydrochloride is sometimes, though inappropriately, designed as *artificial camphor*, and the dihydrochloride as *lemon camphur*.

Hydrates.—Turpentine oil left in contact with water generally changes into a crystalline compound $C_{10}H_{15}.3H_2O$ called *terpin hydrate*, which is more easily obtained by leaving a mixture of 8 pts. turpentine oil, 2 pts. nitric acid of specific gravity 1.25, and 1 pt. alcohol exposed to the air in a shallow vessel. It forms rhombic crystals monodromous, easily soluble in water, alcohol, and ether. It melts below 100° , giving off water, and being converted into a white crystalline mass called *terpin*, having the composition $C_{10}H_{15}.2H_2O$, or $C_{10}H_{15}(OH)_2$, which melts at 103° C. (217.4° F.), and sublimes in slender needles, with de-

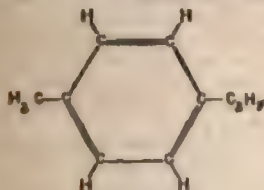
mine at 500° C. (1220° F.) it forms a bromide which, when distilled, yields cymene.

By heating the aqueous solution of terpin with a small quantity of hydrochloric acid, or by boiling the dihydrochloride, $C_{10}H_{16}.2HCl$, with water or alcoholic potash, terpinol, $2C_{10}H_{16}.H_2O$, is obtained as an oil, smelling like hyacinths, and distilling at 168° C. (334.4° F.).

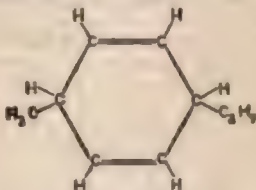
Constitution and Combining Capacity of Turpentine Oil.—The hydrocarbon $C_{10}H_{16}$ acts as a quadrivalent radicle, capable of uniting with four monad atoms, and therefore with two molecules of the acids HCl , HBr , and HI , thereby producing the dihydrochlorides, etc., above mentioned; but, like other tetrad radicles, it can also take up only two monad atoms, producing the monohydrochloride, etc. The same tetrad radicle, by doubling itself, loses two units of equivalence—just as two atoms of carbon when united are satisfied by six, and not by eight atoms of hydrogen—and forms the hydrocarbon, $C_{20}H_{32}$, which is sexvalent, and can therefore form such compounds as $C_{20}H_{32}.3HCl$. Further, this same hexad radicle might form non-saturated compounds containing only four or two monad atoms; in reality, however, only those containing two monad atoms are known, such as $C_{20}H_{32}.HCl$.

If in the several hydrochlorides each atom of chlorine be replaced by hydroxyl, HO , we obtain the formulæ of the several hydrates of turpentine oil; the hydrate corresponding with the hydrochloride, $C_{20}H_{32}.3HCl$, has not, however, been prepared.

The formation of cymene from turpentine, by first converting the latter into the dibromide, $C_{10}H_{16}Br_2$, and then abstracting H_2Br_2 (p. 819), shows that turpentine oil is a hydride of cymene. Now cymene is methyl-propyl-benzene, $C_6H_4.(CH_3).(C_3H_7)$: hence the relation of the two hydrocarbons may be represented by the following formulæ:—



Cymene.



Turpentine oil.

The presence of two lateral chains in the molecule in the position 1 : 4, is in accordance with the formation of terephthalic acid by oxidation of turpentine oil. The other products of its oxidation are likewise in accordance with this view of the constitution of turpentine oil. Other arrangements of the radicles CH_3 and C_3H_7 in the molecule are, however, conceivable, and may perhaps give rise to some of the isomeric modifications of turpentine oil and its congeners. Other modifications may arise from the hydration of other metameric forms of the molecule $C_{10}H_{16}$, e. g., ethyl-dimethyl-benzene and tetra-methyl-benzene.

The formula of turpentine oil above given, in which the double union of one pair of carbon-atoms in cymene is loosened, represents the molecule as saturated. A similar loosening of a second pair would render the molecule bivalent, and therefore capable of taking up 1 mol. of HCl , HBr , Br_2 , etc., and the loosening of the third pair would render it quadrivalent, and capable of uniting with $2HCl$, $2HBr$, etc.

Acids produced by Oxidation of Turpentine-oil.—Turpentine-oil treated with dilute nitric acid yields formic, acetic, butyric, oxalic, terebic, toluar, and terephthalic acids.

Terebic acid, $C_{10}H_{10}O_4$, crystallizes in shining prisms, easily soluble in hot water and alcohol; melts at $175^{\circ}C.$ ($347^{\circ}F.$), and sublimates at a lower temperature. By distillation it is resolved into CO_2 and pyroterebic acid, $C_8H_8O_2$ (p. 716). By boiling with carbonates it forms salts, $C_8H_8M'O_2$, which by the action of strong bases are converted into salts, $C_8H_8M''O_2$, called diaterebates, the acid of which, $C_8H_8O_2$, cannot be obtained in the free state, as, when separated from the salts, it is immediately resolved into water and terebic acid.

Terpin heated to $400^{\circ}C.$ ($752^{\circ}F.$) with soda-lime is converted into terabentilic acid, $C_8H_{10}O_2$, which crystallizes from hot water and alcohol in slender needles melting at $90^{\circ}C.$ ($194^{\circ}F.$), and distilling at $250^{\circ}C.$ ($482^{\circ}F.$). By oxidation with chromic acid mixture, terpin yields terpenylic acid, $C_8H_{10}O_4$, which is monobasic, crystallizes from water with 1 mol. H_2O , and melts in the dehydrated state at $90^{\circ}C.$ ($194^{\circ}F.$).

Volatile or Essential Oils.—The volatile oils obtained from plants by pressure, or by distillation with water, consist either of hydrocarbons, isomeric or polymeric with turpentine oil, or of mixtures of these hydrocarbons with compounds of carbon, hydrogen, and oxygen. Those obtained from aurantiaceous plants are terpenes, distinguished by their fragrant odor. Lemon oil, from the rind of the fruit of *Citrus limonum*, consists mainly of citrene, $C_{10}H_{16}$, a dextrorotatory terpene, almost resembling terebenthene, having a specific gravity of 0.85 at $15^{\circ}C.$ ($59^{\circ}F.$), boiling at 167° or $168^{\circ}C.$ (332.6° or $331^{\circ}F.$). With water it forms a crystallized hydrate resembling terpin; with hydrochloric acid, a dihydrochloride, $C_{10}H_{16}.2HCl$, existing in a solid and liquid modification, and a monohydrochloride, $C_{10}H_{16}.HCl$, apparently susceptible of similar modifications.

Similar oils are obtained from the rind of the sweet orange (*Citrus aurantium*), the bergamot (*C. bergamin*), the bigarade or bitter orange (*C. bigaradia*), the lime (*C. limetta*), the sweet lemon (*C. limon*), and the citron (*C. medica*). Oil of neroli, obtained by distilling orange flowers with water, is probably also a terpene when pure.

The volatile oils of athamanta, beech, birch (from *Dryobalanops Casophora*), camotehous, caraway, camomile, coriander, clove, goment, hup, juniper, imperatoria, laurel, parsley, pepper, savin, thyme, valerian, and others, also the neutral oils of wintergreen (*Gaultheria procumbens*), and cloves, are isomeric with oil of turpentine. The oils of copaiba and cubeba are probably polymeric with it, their molecules containing $C_{20}H_{32}$.

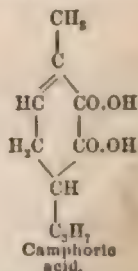
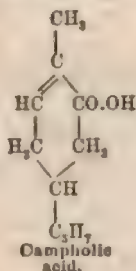
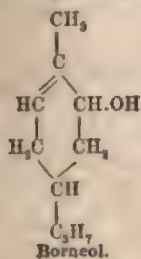
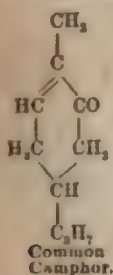
As examples of volatile oils containing an oxygenized constituent mixed with a terpene, may be mentioned valerian oil, which contains valeric acid, $C_5H_{10}O_4$; pelargonium oil, containing pelargonic acid, $C_9H_{18}O_4$; rose oil, containing rosic aldehyde, $C_{11}H_{18}O$; wintergreen oil, containing and methyl salicylate, $C_9H_8O_2$. Some volatile oils consist essentially of aldehydes: thus, bitter almond oil consists of benzoic aldehyde, C_7H_6O ; the oils of cinnamon and cassia contain cinnamic aldehyde, C_9H_8O ; and those of anise, star-anise, fennel, and tarragon, contain anethol, $C_{10}H_{16}O$. These volatile oils which exist ready formed in living plants do not appear to contain any elements besides carbon, hydrogen, and oxygen. Sulphur is found only in certain oils resulting from a kind of fermentation process, as in the volatile oils of mustard and garlic; nitrogen, when it occurs, must be regarded as an impurity resulting from admixed vegetable tissues.

A few volatile oils are found in the bodies of animals—oil of cast, for example.

Most volatile oils are colorless when pure ; they often, however, have a yellow color arising from impurity ; and a few, the oils of wormwood and camomile, for example, have a green or blue color, due to the presence of an oily compound of a very deep blue color, called *cerulein*. They have usually a powerful odor, and a pungent burning taste. When exposed to the air they frequently become altered by slow absorption of oxygen, and assume the character of resins. They mix in all proportions with fat oils, such as linseed, nut, colza, and whale oils, and dissolve freely both in ether and alcohol : from the latter solvent they are precipitated by the addition of water. Volatile oils communicate a greasy stain to paper, which disappears by warming ; by this character any adulteration with fixed oils can be at once detected. Many volatile oils, when exposed to cold, separate into a solid crystalline compound called a *stearoptene*, and a liquid oil, which, for distinction, is sometimes called an *elaeoptene*.

Camphora.

These are oxygenated crystalline compounds, having a peculiar odor. They contain 10 atoms of carbon, and are nearly related to the terpenes, with which they are associated in plants, and by the oxidation of which they appear to be formed. The principal members of the group are common camphor, $C_{10}H_{16}O$, and borneo-camphor or borneol, $C_{10}H_{18}O$, which stand to one another in the relation of a ketone to a secondary alcohol. The constitution of these bodies is not completely established, but their intimate relation to cymene, $C_{10}H_{16}$ (p. 419), and carvacrol, $C_{10}H_{14}O$ (p. 571), **cymene** being produced by heating common camphor with zinc chloride or phosphorus pentasulphide, and carvacrol by heating the same substance with iodine, render it probable that they and their nearest products of oxidation may be represented by the following formulæ :—

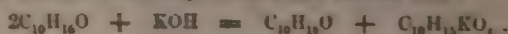


Common Camphor, Laurel Camphor, or Japan Camphor, $C_{10}H_{16}O$, occurs in all parts of the camphor-tree of China and Japan (*Laurus Camphora*), often deposited in distinct crystals ; it is obtained by distilling the woody parts with water, and purified by sublimation. It has been produced artificially in small quantity by oxidation of oil of sage and oil of valerian (i. e., of the terpenes contained in them) by nitric acid ; of turpentine oil by potassium permanganate ; of camphene (from borneol) by platinum-black or chromic acid mixture ; also by oxidation of cymene.

Common camphor is a colorless translucent mass, tough and difficult to powder, having a strong and peculiar taste and smell, and a density of 0.965. Small pieces thrown on water move about with a rotatory motion.

It volatilizes at ordinary temperatures, melts at 175°C . (347°F .), and distils at 204°C . (399.2°F .). It dissolves sparingly in water, easily in alcohol, ether, acetic acid, and volatile oils; and crystallizes from alcohol—also by sublimation—in shining strongly refractive crystals. The alcoholic solution is dextro-rotatory: $[\alpha] = +47.4^{\circ}$.

By distillation over fused zinc chloride, or with phosphoric anhydride, camphor is resolved into water and cymene: $\text{C}_{10}\text{H}_{16}\text{O} = \text{C}_{10}\text{H}_{16} + \text{H}_2\text{O}$, considerable quantities of mesitylene, toluene, xylene, and other C_9 -carbons being, however, formed at the same time. The formation of cymene takes place more definitely when camphor is distilled with phosphorus pentasulphide, thiocymene, $\text{C}_{10}\text{H}_{16}\text{SH}$, being formed at the same time. Heated with iodine ($\frac{1}{2}$ part) it yields carvacrol. By heating with alcoholic potash it is resolved into borneol and camphoric acid, just as benzaldehyde is resolved into benzyl alcohol and benzoic acid:

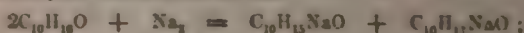


By heating with nitric acid, camphor is converted into camphoric and camphoronic acids; heated to 400°C . (752°F .) with soda-lime, it yields camphoric acid, $\text{C}_{10}\text{H}_{14}\text{O}_2$.

Camphor, heated with bromine to 110° – 120°C . (230° – 240°F .), yields crystalline $\text{C}_{10}\text{H}_{15}\text{BrO}$ (m. p. 75°C ., 167°F ., b. p. 275°C ., 527°F .), and $\text{C}_{10}\text{H}_{14}\text{Br}_2\text{O}$ (m. p. 214°C ., 417.2°F ., b. p. 285°C ., 543°F .). Camphor dissolved in chloroform takes up bromine, forming $\text{C}_{10}\text{H}_{16}\text{OBr}_2$, easily converted into $\text{C}_{10}\text{H}_{15}\text{BrO}$.

Camphor treated with hypochlorous acid, yields monochloro-camphor, $\text{C}_{10}\text{H}_{15}\text{ClO}$, a crystalline mass melting at 95°C . (203°F .), and converted by heating with alcoholic potash into *orycamphor*, $\text{C}_{10}\text{H}_{16}\text{O}_2$, which sublimes in needles melting at 137°C . (278.6°F .). Camphor heated with HCl yields the compounds $\text{C}_{10}\text{H}_{16}\text{Cl}_2$ and $\text{C}_{10}\text{H}_{15}\text{Cl}$, easily converted, by abstraction of hydrogen chloride, into cymene.

A solution of camphor in toluene heated with sodium, deposits a mixture of sodium-camphor and sodium-borneol:



and these compounds treated with CH_3I and $\text{C}_2\text{H}_5\text{I}$, yield methyl and ethyl-derivatives of camphor and borneol: $\text{C}_{10}\text{H}_{15}(\text{C}_2\text{H}_5)_2\text{O}$ is a liquid boiling at 210°C . (416°F .).

When the sodium-compounds are treated at 100° with CO_2 , the sodium salts of camphocarmonic acid, $\text{C}_{10}\text{H}_{15}\text{O}(\text{CO}_2\text{H})$, and borneocarmonic acid, $\text{C}_{10}\text{H}_{17}\text{O}(\text{CO}_2\text{H})$, are produced; and on treating the resulting mass with water, borneol separates from the toluene which floats on the surface, and the aqueous solution mixed with hydrochloric acid yields a precipitate of camphocarmonic acid. This acid crystallizes from alcohol in small prisms, melting at 115°C . (241.4°F .), and is easily resolved into CO_2 and camphor.

Isomides of Camphor.—By distilling the essential oil of feverfew (*Fycthrum Parthenium*), and collecting apart the portion which passes over between 200° and 220°C . (392° and 428°F .), an oil is obtained, which, on cooling, deposits a crystalline substance resembling common camphor in every respect, except that its action on polarized light is exactly equal and opposite. $[\alpha] = -47.4^{\circ}$. The essential oils of many labiate plants, as *mentha*, *marjoram*, lavender, and sage, often deposit a substance having the

composition and all the properties of common camphor, excepting that it is inactive to polarized light.

Absinthol, $C_{10}H_{16}O$, from oil of wormwood (*Artemisia Absinthium*), is liquid, boils at $195^{\circ}C.$ ($383^{\circ}F.$), and is converted by P_2S_5 into cymene. Similar liquid camphors are obtained by oxidation of certain terpenes, as the oils of orange and nutmeg. A polymeric camphor, caryophyllin, $C_{20}H_{32}O_8$ (m. p. above $300^{\circ}C.$, $572^{\circ}F.$), is contained in cloves.

Borneo-camphor or **Borneol**, $C_{10}H_{18}O = C_{10}H_{17}.OH$, occurs in *Dryobalanops Camphora*, a tree growing in Borneo and Sumatra: it is formed artificially by heating common camphor with alcoholic potash, or treating it with sodium (p. 966).

Borneol is very much like common camphor, has a camphorous and peppery odor, melts at $198^{\circ}C.$ ($388.4^{\circ}F.$), and boils at $212^{\circ}C.$ ($413.6^{\circ}F.$). Its alcoholic solution is dextrorotatory. By heating with nitric acid it is converted, first into common camphor, then into camphoric and camphoronic acids. By heating with P_2O_5 , it is resolved into water and borneene, $C_{10}H_{16}$, apparently identical with the terpene contained in ordinary camphor oil (from *Laurus Camphora*), and in valerian oil; when left in contact with potash-lye, it is reconverted into borneol.

Borneol is an alcohol, yielding compound ethers when heated to about $200^{\circ}C.$ ($392^{\circ}F.$) with organic acids. The stearic ether, $C_{10}H_{17}.O.C_{18}H_{35}O_2$, is a colorless, viscid liquid, which gradually solidifies. By the action of PCl_5 at ordinary temperatures, or by heating in a sealed tube with HCl , borneol is converted into the chloride, $C_{10}H_{17}Cl$, a crystalline substance melting at $146^{\circ}C.$ ($294.8^{\circ}F.$), and very much like the solid modification of the hydrochloride of turpentine-oil, with which it is isomeric.

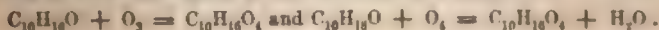
Isomeric with borneol are the liquid camphors contained in the oils of hops, Indian geranium, cajeput, coriander, and *Osmitopsis asteriscoides*. Homologous with borneol is Patchouli-camphor, $C_{15}H_{26}O$, contained in oil of patchouli: it is a crystalline mass, melting at $54^{\circ}-55^{\circ}C.$ ($129.2^{\circ}-131^{\circ}F.$), boiling at $296^{\circ}C.$ ($564.8^{\circ}F.$).

Mint-camphor or **Menthhol**, $C_{10}H_{20}O$, occurs, together with a terpene, in oil of peppermint (*Mentha piperita*), and separates in crystals on cooling the oil. It melts at $36^{\circ}C.$ ($96.8^{\circ}F.$), boils at $213^{\circ}C.$ ($415.4^{\circ}F.$); turns the plane of polarization to the left; forms compound ethers with acids; is converted by PCl_5 or HCl into the liquid chloride, $C_{10}H_{19}Cl$, and by distillation with P_2O_5 or $ZnCl_2$ into liquid menthene, $C_{10}H_{18}$, which boils at $163^{\circ}C.$ ($325.4^{\circ}F.$).

Acids produced by Oxidation of Camphor.

Campholic Acid, $C_{10}H_{16}O_2$, obtained by passing camphor-vapor over heated soda-lime, or by the action of potassium on a solution of camphor in petroleum, crystallizes from alcohol in prisms or scales, slightly soluble in water, melting at $95^{\circ}C.$ ($203^{\circ}F.$), and easily subliming; converted by nitric acid into camphoric and camphoronic acids; resolved by distillation with phosphoric anhydride into H_2O , CO_2 , and campholene, C_9H_{12} , boiling at $135^{\circ}C.$ ($275^{\circ}F.$).

Camphoric Acid, $C_{10}H_{16}O_4 = C_9H_{14}(CO_2H)_2$, is obtained by prolonged boiling of common camphor or borneol with nitric acid:



It is dextro- or levo-rotatory according to the variety of camphor used in its preparation; a mixture of the dextro- and levo-rotatory camphors in equal quantities yields an inactive camphoric acid.

Dextrocamphoric acid crystallizes from hot water in colorless laminae, easily soluble in alcohol, melting at 175° – 175° C. (347 – 353.4° F.), and decomposing at a high temperature into water and camphoric anhydride, $C_{10}H_{14}O_3$, which sublimes at 130° C. (260° F.) in shining needles, melts at 217° C. (422.6° F.), and boils at 270° C. (518° F.).

The acid is bibasic. The calcium and barium salts are easily soluble in water, and crystallize well. The calcium salt is resolved by heat into carbonate and camphor-phonone: $C_{10}H_{14}O_4Ca = CO_2Ca + C_9H_{14}O$, isomeric with phonone from acetone (p. 680), a liquid which boils at 208° C. (406.4° F.), and does not yield cymene when heated with phosphoric anhydride.

Camphoric acid heated with water to 150° – 200° C. (302° – 392° F.) is converted into two inactive modifications, isocamphoric and paracamphoric acids. The former crystallizes in slender needles melting at 113° C. (235.4° F.).

The acid, or its anhydride, heated with bromine to 130° – 150° C. (266° – 302° F.), yields bromocamphoric anhydride, $C_{10}H_{13}BrO_3$, which crystallizes in needles melting at 215° C. (419° F.), and, when boiled with water, is converted into the monobasic acid, $C_{10}H_{14}O_4$ (oxycamphoric anhydride or camphoric acid), melting at 201° C. (339.8° F.), and subliming at 110° C. (230° F.). This acid, or oxyanhydride, heated with water to 161° C. (357.8° F.), yields a hydrocarbon C_9H_{16} , boiling at 120° C. (248° F.).

Camphoric acid, $C_9H_{12}O_5$, and Oxycamphoric acid, $C_9H_{12}O_6$, are contained in the mother-liquor of the preparation of camphoric acid. The former crystallizes from water in slender needles with 1 mol. H_2O , which it gives off at 110° C. (230° F.); melts in the dehydrated state at 115° C. (239° F.); and distils without decomposition. The oxy-acid, $C_9H_{10}O_6$, crystallizes in long prisms melting at 164.5° C. (328.1° F.).

Resins and Balsams.

Common resin, or *colophony*, is perhaps the best example of the class. It is the resinous substance which remains when turpentine or pine-resin is heated till the water and volatile oil are expelled, and consists essentially of sylvic or abietic acid, $C_{20}H_{30}O_4$. On boiling the resin for a long time with alcohol of about 80 per cent., filtering, and adding a little water, the sylvic acid separates in the crystalline state. It crystallizes from alcohol in laminae melting at 129° C. (264.3° F.). It is monobasic, its alkali-salts are soluble and crystallizable.

An acid called pimaric acid, isomeric with sylvic acid, is obtained from the turpentine of the *Pinus maritima* of Bordeaux.

Lac is a very valuable resin, much harder than colophony, and easily soluble in alcohol: three varieties are known in commerce—viz., *mastic*, *seed-lac*, and *shellac*. It is used in varnishes, and in the manufacture of hats, and very largely in the preparation of sealing-wax, of which it forms the chief ingredient. Crude lac contains a red dye called *lac dye*, which is partly soluble in water. Lac dissolves in considerable quantity in a hot solution of borax; Indian ink, rubbed up with this liquid, forms an excellent *label-ink* for the laboratory, as it is unaffected by acid vapors, and, when once dry, becomes nearly insoluble in water.

Mastic, dammar-resin, and sandarac are resins largely used by the varnish maker. Dragon's blood is a resin of deep-red color. Copal is also a very

valuable substance: it differs from the other resins in being but slowly dissolved by alcohol and essential oils. It is miscible, however, in the melted state with oils, and is thus made into varnish. *Amber* appears to be a fossil resin; it is found accompanying brown-coal or lignite.

Most resins, when exposed to destructive distillation, yield oily pyro-products, usually consisting of hydrocarbons.

Caoutchouc, or *India-rubber*, the thickened milky juice of several species of *Ficus*, *Euphorbia*, and other trees growing in tropical countries, is essentially a mixture of several hydrocarbons isomeric or polymeric with turpentine oil. When pure it is nearly white, the dark color of commercial caoutchouc being due to the effects of smoke and other impurities. It is softened but not dissolved by boiling water: it is also insoluble in alcohol. In pure ether, rectified petroleum, and coal-tar oil, it dissolves, and is left unchanged on the evaporation of the solvent. Oil of turpentine also dissolves it, forming a viscid, adhesive mass, which dries very imperfectly. At a temperature a little above the boiling point of water, caoutchouc melts, but never afterwards returns to its former elastic state. Few chemical agents affect this substance: hence its great use in chemical investigations, for connecting apparatus, etc. By destructive distillation it yields a large quantity of a thin, volatile, oily liquid, of naphtha-like odor, called *caoutchoucine*, which dissolves caoutchouc with facility. This oil, according to Mr. Greville Williams, is composed of two polymeric hydrocarbons: caoutchicin, $C_{10}H_{16}$, boiling at $171^{\circ}C.$ ($339.8^{\circ}F.$), and isoprene, C_5H_8 , boiling at $37^{\circ}C.$ ($98.6^{\circ}F.$).

Caoutchouc combines with variable proportions of sulphur. The mixtures thus obtained are called *vulcanized India-rubber*: they are more permanently elastic than pure caoutchouc.

Vulcanite, or *Ebonite*, is caoutchouc mixed with half its weight of sulphur, and hardened by pressure and heating. It is very hard, takes a high polish, and is used for making combs, knife-handles, buttons, etc. It is also especially distinguished by the large quantity of electricity which it evolves when rubbed: hence it makes an excellent material for the plates of electrical machines.

Gutta-percha, the hardened milky juice of *Isanandra gutta*, a large tree growing in Malacca and many of the islands of the Eastern Archipelago, is similar in composition to caoutchouc, and resembles it in many of its properties, but is harder and less elastic. It is quite insoluble in, and impervious to water, and being also an excellent electric insulator, is extensively used as a casing for submarine telegraph wires. By dry distillation it yields isopene, caoutchicin, and a heavy oil called *heveene*, probably polymeric with these bodies.

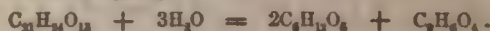
Balsams are natural mixtures of resins with volatile oils. They differ very greatly in consistence, some being quite fluid, others solid and brittle. By keeping, the softer kinds often become hard. Balsams may be conveniently divided into two classes—viz., those which, like *common* and *Venice turpentine*, *Canada balsam*, *Copaiba balsam*, etc., are merely natural varnishes, or solutions of resins in volatile oils, and those which contain benzoic or cinnamic acid in addition, as *Peru* and *Tolu balsams*, and the solid resinous *benzoin*, commonly called *gum-benzoin* (p. 894).

Glucosides.

This name is given to a class of bodies, very widely diffused in the vegetable kingdom, which are resolved by boiling with dilute acids or alkalies, or by the action of ferments, into glucoses (mostly dextrose), and some other

substance. They are therefore analogous in constitution to the artificial glucosides which Berthelot obtained by heating glucose with organic acids (p. 624); none of them have, however, been formed artificially. The following are the most important:—

Æsculin, $C_{21}H_{34}O_{13}$, is a crystalline fluorescent substance obtained from the bark of the horse-chestnut and other trees of the genera *Æsculus* and *Pædia*. It has a bitter taste, is slightly soluble in water and alcohol, more soluble in the same liquids at the boiling heat, nearly insoluble in ether. It is colored red by chlorine. By boiling with hydrochloric or dilute sulphuric acid, it is resolved into glucose and a bitter crystalline substance called *æsculetin*, $C_9H_8O_4$:

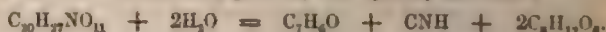


The aqueous solution of *æsculin* is highly fluorescent, the reflected light being of a sky-blue color. Nearly the same fluorescent tint is exhibited by an infusion of horse-chestnut bark. The color of the latter is, however, slightly modified by the presence of another substance, *paviin*, which exhibits a blue-green fluorescence; it may be separated from *æsculin* by its greater solubility in ether. *Æsculin* and *paviin* appear to exist together in the barks of all species of *Æsculus* and *Pædia*,—*æsculin* being more abundant in the former, and *paviin* in the latter.

Amygdalin, $C_{20}H_{27}NO_{11}$, is a crystalline body existing in bitter almonds, the leaves of cherry-laurel (*Cerasus Laurocerusus*), and many other plants which by distillation yield hydrocyanic acid and bitter-almond oil, C_7H_8O . To prepare it, the almonds, previously freed from fixed oil by pressure, are exhausted with boiling alcohol, and the concentrated solution is mixed with ether.

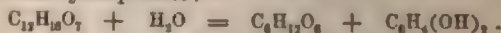
Amygdalin crystallizes from alcohol in white shining laminae, has a bitter taste, dissolves easily in water and in hot alcohol; from water it crystallizes in prisms containing $3H_2O$.

By boiling with dilute acids, and by contact with water and emulsin or *synaptase*, a ferment contained in bitter almonds, amygdalin is resolved into bitter almond oil, glucose, and hydrocyanic acid:



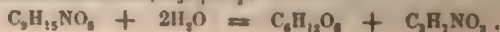
When amygdalin is boiled with alkalis, its nitrogen is separated as ammonia, and amygdalic acid, $C_{10}H_{25}O_{13}$, is formed, which by boiling with dilute acids is resolved into mandelic acid and glucose.

Arbutin, $C_{12}H_{16}O_7$, from the leaves of the bear-berry (*Arbutus uva ursi*), crystallizes in slender needles, having a bitter taste, and dissolving easily in water, alcohol, and ether. By boiling with dilute acids it is resolved into glucose and hydroquinone:



It dissolves in strong nitric acid, forming $C_{12}H_{14}(NO_2)_2O_7$, which splits up into glucose and dinitrohydroquinone.

Chitin, $C_8H_{13}NO_3$, is the substance which forms the elytra and integuments of insects, and the carapaces of crustaceans. It is best prepared by boiling the wing-cases of cockchafers with water, alcohol, ether, acetic acid, and alkalis in succession, as long as anything is dissolved out by each. According to Stadelcr, it is resolved by boiling with dilute acids into glucose and lactamide, $C_5H_7NO_2$:

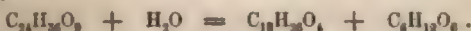


Coniferin, $C_{16}H_{27}O_6$, occurs in the cambial juice of coniferous plants, and separates therefrom on concentration in stellate groups of pointed needles, having a satiny lustre, and containing $2H_2O$, which they lose by efflorescence. By boiling with dilute acids it is resolved into dextrose and a resin; in contact with emulsin, into dextrose and coniferyl alcohol. By oxidation with chromic acid mixture it yields vanillin (p. 871).

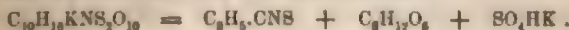
Convolvulin, $C_{31}H_{55}O_{16}$, is obtained from jalap root (*Convolvulus schiedanus*) by extraction with alcohol. It is a gummy mass having a strong purgative action; dissolves in alkalies as convolvulic acid, $C_{31}H_{53}O_{17}$; resolved by acids and by emulsin into dextrose and convolvulinol, $C_{15}H_{27}O_8$, which is converted by alkalies into convolvulinolic acid, $C_{15}H_{25}O_8$. This latter is a monobasic acid, which is oxidized by nitric acid to ipomasic acid, $C_{10}H_{18}O_4 = C_6H_{16}(CO_2H)_2$, isomeric with sebacic acid (p. 752).

Jalappin, $C_{31}H_{55}O_{16}$, from the root of *Convolvulus orizabensis*, closely resembles convolvulin, and yields analogous products of decomposition.

Glycyrrhizin, $C_{42}H_{76}O_{19}$; *Liquorice-sugar*.—The root of the common liquorice yields a large quantity of a peculiar sweet substance, which is soluble in water, but does not crystallize: it cannot be made to ferment. Glycyrrhizin forms difficultly soluble compounds with acids; it is precipitated from its solution by lead, calcium, and barium salts, the precipitate consisting of glycyrrhizin in combination with the base. When boiled with dilute acids, it splits into a resinous body called glyceretin, $C_{18}H_{32}O_8$, and glucose:



Myronic Acid, $C_{10}H_{19}NS_2O_{10}$, an acid existing as a potassium salt in the seed of black mustard, is resolved by the action of *myrosin*, an albuminous ferment likewise contained in the seeds, into volatile oil of mustard (allyl sulphocyanate), glucose, and sulphuric acid:



Phlorizin, $C_{21}H_{34}O_{10} \cdot 2H_2O$, is a substance bearing a great likeness to salicin, found in the root-bark of the apple and cherry tree, and extracted by boiling alcohol. It forms fine, colorless, silky needles, soluble in 1000 parts of cold water, but freely dissolved by that liquid when hot; it also dissolves easily in alcohol. Dilute acids convert phlorizin into glucose and a crystallizable sweet substance called phloretin:



Phlorizin, fused with potash, yields phloretic acid, $C_9H_{10}O_3$, a beautifully crystalline acid, homologous with salicylic and anisic acids, together with phloroglucin, $C_6H_4O_3$.

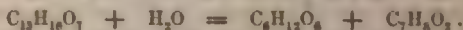
Quercitrin is a crystallizable yellow coloring matter occurring in quercitron bark, the bark of *Quercus infectoria*, whence it is extracted by boiling with water. Its composition has been variously stated; indeed, it is by no means certain that the so-called quercitrins examined by different chemists were really identical substances. According to Hlasiwetz and Pfandler, it contains $C_{33}H_{50}O_{17}$, and is resolved by boiling with dilute acids into another yellow crystalline body called quercetin, and isodulcitol (p. 619):



Salicin, $C_{13}H_{16}O_7$, is a crystallizable bitter substance contained in the leaves and young bark of the poplar, willow, and several other trees. It may be prepared by exhausting the bark with boiling water, concentrating the solution to a small bulk, digesting the liquid with powdered lead oxide, and then, after freeing the solution from lead by a stream of sulphuretted hydrogen gas, evaporating till the salicin crystallizes out on cooling. It is purified by treatment with animal charcoal and recrystallization.

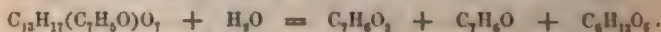
Salicin forms small, white, silky needles, having an intensely bitter taste, but no alkaline reaction. It melts and decomposes by heat, burning with a bright flame, and leaving a residue of charcoal. It is soluble in 5.6 parts of cold water, and in a much smaller quantity when boiling hot. Oil of vitriol colors it deep-red. When distilled with a mixture of potassium bichromate and sulphuric acid, it yields salicylal and other products.

Salicin, under the influence of emulsin or synaptase of sweet almonds, is resolved into glucose and saligenin, $C_7H_8O_2$ (p. 884).



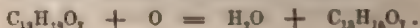
Salicin yields, with *chlorine*, substitution products which are decomposed by synaptase in the same manner as salicin itself, yielding chlorosaligenin, $C_7H_7ClO_2$, and dichlorosaligenin, $C_7H_6Cl_2O_2$. Dilute *nitric acid* converts salicin into helicin. With strong nitric acid, at a high temperature, nitrosalicylic acid, $C_7H_5(NO_2)O_3$, is produced.

Populin, $C_{30}H_{42}O_{16}$, is a substance resembling salicin in appearance and solubility, but having a sweet pungent taste. It is found accompanying salicin in the bark and leaves of the aspen. It has the composition of benzoyl-salicin, $C_{13}H_{17}(C_7H_5O)_7$, and when heated with dilute acids, is resolved into benzoic acid and the products of decomposition of salicin, namely, saliretin and glucose:

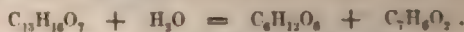


With potassium dichromate and sulphuric acid, populin yields a considerable quantity of salicylal.

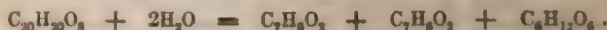
Helicin, $C_{13}H_{16}O_7$, is a white, crystalline, slightly bitter substance, produced by the action of very dilute nitric acid upon salicin:



It is slightly soluble in cold, freely soluble in boiling water, and is resolved by the action of synaptase, or of acids or alkalies at the boiling heat, into glucose and salicylal:



Benzohelicin, $C_{30}H_{42}O_{16}$, or $C_{13}H_{15}(C_7H_5O)_7$, produced by the action of dilute nitric acid on benzo-salicin, is resolved in like manner into benzoic acid, salicylal, and glucose:



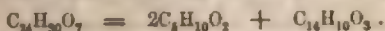
Bitter Principles of Plants.

These are neutral bodies of somewhat indefinite chemical character, which cannot at present be included in any of the preceding groups.

Aloin is a constituent of aloe, the inspissated juice of various species of aloe, and is extracted by treating the aloe with water. It is easily soluble in warm water and alcohol, and crystallizes in slender needles. It is very bitter and strongly purgative.

Aloin from Barbadoes aloe has the composition $C_{17}H_{18}O_7$; that from Natal aloe is $C_{21}H_{22}O_{15} = 2C_{17}H_{18}O_7 + H_2O$. The former (barbaloin) heated with nitric acid yields aloetic acid, $C_{14}H_8(NO_2)_4O_8$, together with oxalic, picric, and chrysammic acids; the latter (nataloin) yields picric and oxalic acids, but no chrysammic acid.

Athamantin, $C_{24}H_{30}O_7$, obtained from the roots of *Athamanta Oreoselinum* by extraction with ether, crystallizes from alcohol and ether in slender needles melting at $79^\circ C.$ ($174.2^\circ F.$). By boiling with hydrochloric acid it is resolved into valeric acid and oreoselone, $C_{14}H_{16}O_2$:



By further boiling with dilute hydrochloric acid, oreoselone is converted into oreoselin, $C_{14}H_{12}O_4$.

Cantharidin, $C_8H_6O_2$, is the vesicating principle of Spanish flies and some other insects, and may be extracted with ether. It crystallizes in four-sided prisms or laminae, dissolves in hot alcohol and ether, melts at $250^\circ C.$ ($482^\circ F.$), and sublimes at a lower temperature. Heated with alkalis it dissolves, forming salts of cantharidic acid, e. g., $C_8H_7KO_3$, from which acids reprecipitate cantharidin.

Carotin, $C_{40}H_{56}O$, a substance deposited in small crystals in the cells of the red carrot, crystallizes from alcohol in red-brown cubes melting at $168^\circ C.$ ($334.4^\circ F.$).

Peucedanin, $C_{24}H_{32}O_8$, from the roots of *Peucedanum officinale*, crystallizes from alcohol in shining prisms melting at $75^\circ C.$ ($167^\circ F.$). Boiled with alcoholic potash it is resolved into angelic acid and oreoselin.

Picrotoxin, $C_{12}H_{14}O_6$, is extracted by alcohol from cocculus grains (the seeds of *Menispermum Cocculus*); crystallizes in slender needles; very bitter and poisonous.

Santonin, $C_{15}H_{14}O_3$, is the active principle of wormseed (from *Artemisia santonica*), from which it may be extracted by boiling with milk of lime and precipitation by hydrochloric acid. It crystallizes from hot alcohol in shining prisms melting at $170^\circ C.$ ($338^\circ F.$); dissolves in alkalis, forming salts of santoninic acid, $C_{15}H_{12}O_4$.

Coloring Matters.

The most important coloring matters of vegetable origin, viz., the indigo and madder dyes, have already been described.

Brazilin, $C_7H_{10}O_7$, the coloring matter of Brazil wood, crystallizes in small yellow prisms, which dissolve in alcohol with reddish-yellow, in

alkalies with crimson color; the solution is decolorized by sulphurous acid and zinc-dust. Nitric acid converts brazilin into trinitroresorcin.

Carminic acid, $C_{17}H_{10}O_{10}$, occurs in the flowers of *Munzchia dulcis*, and a few other plants, and more abundantly in cochineal, an insect (*Coccus Cacti*) living on various species of cactus. To obtain the carminic acid, the aqueous decoction of the insects is precipitated by lead acetate, and the pure lead carminate washed and decomposed by hydrogen sulphide; the coloring matter thus separated is again submitted to the same treatment. A solution of carminic acid is thus obtained, which is evaporated to dryness, redissolved in absolute alcohol, digested with crushed lead carbonate, whereby a small quantity of phosphoric acid is separated, and lastly, mixed with ether, which separates a trace of a nitrogenous substance. The residue now obtained on evaporation is pure carminic acid.

It is a purple-brown mass, yielding a fine red powder, soluble in water and alcohol in all proportions, slightly soluble in ether. It dissolves without decomposition in concentrated sulphuric acid, but is readily attacked by chlorine, bromine, and iodine, which change its color to yellow. It resists a temperature of $136^{\circ}C.$ ($276.8^{\circ}F.$), but is charred when heated more strongly. Carminic acid is bibasic, and forms colored salts. By boiling with dilute sulphuric acid it is resolved into a non-fermentable sugar and carmine-red, $C_{11}H_{12}O_7$. Boiled with nitric acid it yields oxalic acid and nitro-cresotic acid, $C_6H_2(NO_2)_2O_2.H_2O$, which crystallizes from water in large shining plates, and when heated with water to 180° is resolved into CO_2 and trinitro-cresotic acid, $C_6(NO_2)_3((CH_2)(OH).CO_2H$. Cochineal is used for giving a red color to silk and wool.

Carthamin, $C_{14}H_{16}O_7$, is the red coloring matter of the petals of the safflower (*Carthamus tinctorius*). It is prepared by exhausting the flowers with cold water to remove a yellow substance, and treating the residue with a dilute solution of sodium carbonate; this dissolves the carthamin, which may be precipitated by acetic acid as a dark red powder having a green metallic lustre when dry. It dissolves in alcohol and alkalies with a fine red color, which, however, is very fugitive. By fusion with potash it yields paraoxybenzoic and oxalic acids. Carthamin is used for dyeing silk, and as a cosmetic.

Chlorophyll, or Leaf-green, is contained, together with wax and other substances, in the chlorophyll granules which occur in all the green parts of plants, and may be obtained by exhausting these organs with ether, and treating the residue with alcohol, in which the chlorophyll is easily soluble. It dissolves also in strong hydrochloric acid. Its composition is not known, but iron appears to be an essential constituent.

Curcumin, $C_{18}H_{16}O_2$, is the coloring matter of turmeric. It dissolves easily in alcohol and ether, sparingly in carbon sulphide, and in cold benzene, and is best extracted from the root by boiling benzene. It forms orange-yellow crystals, and exhibits in solution a green fluorescence. From its brown red solution in alkalies, it is precipitated by acids as a yellow powder. The yellow tint of paper stained with turmeric is turned brown by alkalies and restored by acids.

Euxanthic acid, $C_{18}H_{16}O_{10}$, occurs as a magnesium salt in *Neraris Indian yellow*, a yellow coloring matter of unknown origin imported from India and China. The euxanthic acid is obtained by digesting the mass with dilute hydrochloric acid, and exhausting with alcohol. It dissolves easily in alcohol and ether, and crystallizes in shining yellow prisms. Euxanthic acid is resolved by strong sulphuric acid into a smoky-red substance and euxanthone, $C_{15}H_{12}O_4$, which sublimes in yellow needles. Euxanthone fused with potash yields first oxanthonic acid, $C_{15}H_{10}O_4$,

then hydroquinone. Strong nitric acid converts it into trinitroresorcin, and, on the other hand, resorcin heated with oxalic and sulphuric acid, appears to yield euxanthone.

Hematoxylin, $C_{16}H_{14}O_6$, the coloring matter of logwood, crystallizes with 3 mol. H_2O in pale-yellow prisms; has a sweetish taste; dissolves easily in water, alcohol, and ether, forming dextro-rotatory solutions. With acetyl chloride, it forms $C_{16}H_{14}(C_2H_3O)_6O_6$.

By exposure to the air in ammoniacal solution, it is converted into hematein-ammonia, $C_{16}H_{11}(NH_4)O_6$, which, on spontaneous evaporation, is deposited in dark violet crystals. Acetic acid added to the solution throws down hematein, $C_{16}H_{13}O_6$, as a red-brown precipitate, having a metallic lustre when dry, and dissolving in alkalis with a fine violet-blue color. Sulphurous acid and other reducing agents reconvert hematein into hematoxylin. The latter, fused with potash, yields pyrogallol.

Alkaloids.

This term is sometimes used as a general name for organic bases, but it is more especially applied to those which occur ready formed in the bodies of plants and animals, and those which are produced by the destructive distillation of complex organic bodies. All these bases, like the amines already described, are derivatives of ammonia, but their molecular structure is for the most part unknown. Those which are free from oxygen are volatile; those which contain that element are decomposed by distillation.

NON-OXIDISED VOLATILE BASES.

Pyridine Bases, $C_nH_{2n-5}N$.—These bases, metameric with aniline and its homologues, are contained in coal-tar naphtha, and in the volatile oil called Dippel's oil (*Oleum animale Dippelii*), obtained by the distillation of bones and other animal matters. They are all liquid at ordinary temperatures, and react as tertiary monamines. Their formulæ and boiling points are as follows:—

| | | R. P. | | | R. P. |
|------------|----------------|-------|------------|-------------------|-------|
| Pyridine, | C_5H_5N , | 117° | Parvoline, | $C_9H_{13}N$, | 188° |
| Picoline, | C_6H_7N , | 133° | Coridine, | $C_{10}H_{15}N$, | 211° |
| Lutidine, | C_7H_9N , | 154° | Rubidine, | $C_{11}H_{17}N$, | 230° |
| Collidine, | $C_8H_{11}N$, | 179° | Viridine, | $C_{12}H_{19}N$, | 251° |

Pyridine is said to be formed artificially by heating amyl nitrate with phosphoric oxide: $C_5H_{11}NO_3 - 3H_2O = C_5H_5N$. When heated with sodium it is converted into dipyrindine, $C_{10}H_{10}N_2$, a crystalline base which melts at 108° C. (226.4° F.), and sublimes at higher temperatures in needle-shaped crystals.

Picoline (metameric with aniline), first obtained by Anderson from coal-tar naphtha, is a mobile liquid, having a strong, persistent odor, and acid, bitter taste: sp. gr. 0.995. It remains liquid at -18° C. (0.4° F.), and volatilizes quickly in the air. It is strongly alkaline to test-paper, mixes with water in all proportions, and forms crystallizable salts.

Dippel's oil likewise contains methylamine and several of its homologues.

Chinoline Bases, $C_nH_{2n-11}N$.—Three bases of this series, viz.:

| | | |
|------------|--------------|--------------|
| C_9H_9N | $C_{10}H_9N$ | $C_{11}H_9N$ |
| Chinoline. | Lepidine. | Cryptidine. |

are produced by distillation of quinine, cinchonine, and a few other natural alkaloids, with potassium hydroxide; and other bases isomeric with them, viz., *leucoline*, C_9H_7N , *iridoline*, $C_{10}H_9N$, etc., are contained in coal-tar naphtha, and distil over after the pyridine bases (above $200^{\circ}C.$, $392^{\circ}F.$). They are oily liquids insoluble in water, easily soluble in alcohol and ether. They are tertiary amines, yielding ammonium-bases when treated with ethyl iodide and silver oxide. These salts are crystalline, and easily soluble.

Chinoline, C_9H_7N , is a mobile, strongly refracting liquid, boiling at $238^{\circ}C.$ ($460.4^{\circ}F.$), and having a sp. gr. of 1.081 at $4^{\circ}C.$ Heated with anil iodide, it forms the compound $(C_9H_7)(C_6H_5)NI$, which is converted by heating with potash into cyanine, $C_{15}H_{11}N$, a fine blue dye-stuff, which crystallizes in green metallic lustrous plates, and dissolves with blue color in alcohol. A similar blue color is obtained with lepidine, and a mixture of the two has been used for dyeing silk.

Leucoline, C_9H_7N , from coal-tar oil, boils at about $220^{\circ}C.$ ($428^{\circ}F.$), and does not yield cyanine.

Lepidine, from cinchonine, boils at $266^{\circ}-270^{\circ}C.$ ($510.8^{\circ}-518^{\circ}F.$); the isomeric base from coal-tar oil boils at $252^{\circ}-257^{\circ}C.$ ($485.6^{\circ}-494.6^{\circ}F.$).

Conine, $C_8H_{15}N$, is contained in hemlock (*Conium maculatum*), especially in the seeds, and is obtained therefrom by distillation with potash-lye. It is a colorless oily liquid, having a pungent, stupefying odor, and is very poisonous. Sp. gr. 0.89. Boiling point $168^{\circ}C.$ ($334.4^{\circ}F.$). It dissolves easily in alcohol and ether, sparingly in water, and forms crystalline deliquescent salts, which, like the base itself, turn brown in contact with the air. With oxidizing agents conine yields butyric acid.

Conine is a secondary monamine. Treated with ethyl iodide it yields successively two iodine-compounds—namely, $C_9H_{15}(C_2H_5)NI$ and $C_8H_{14}(C_2H_5)_2NI$. The latter is converted by silver oxide into a soluble base.

Puraconine, isomeric with conine, is formed artificially by heating normal butyric aldehyde, C_4H_8O , with alcoholic ammonia—whereby *debutyridine* is obtained, having the composition $C_8H_{17}NO[=2C_4H_8O + NH_3 - H_2O]$,—and subjecting this base to dry distillation: $C_8H_{17}NO - H_2O = C_8H_{15}N$. It is a violent poison, acting in the same manner as the natural base. But it is less soluble in water, more expansible by heat, and exhibits somewhat different reactions with hydrochloric acid, silver nitrate, and gold chloride. With ethyl iodide it forms the iodide of an ammonium-base, convertible by silver oxide into a strongly alkaline, bitter syrupy liquid: hence it is a tertiary monamine.

Closely allied to conine is *conhydrine*, $C_8H_{17}NO$, a crystalline base, extracted from hemlock flowers. When distilled with anhydrous phosphoric acid, it splits into conine and one molecule of water.

Nicotine, $C_{10}H_{14}N_2$, exists in the seeds and leaves of various kinds of tobacco, from which it may be obtained by extraction with dilute sulphuric acid, and distillation of the concentrated extract with potash-lye. It is a colorless oil, having a density of 1.048, boiling with partial decomposition at $250^{\circ}C.$ ($482^{\circ}F.$), without decomposition in a stream of hydrogen at $1500^{\circ}-2000^{\circ}C.$ ($3020^{\circ}-3930^{\circ}F.$). It turns brown in the air, has a very stupefying odor, and is very poisonous. It is a monoacid base, forming very soluble salts, which crystallize with difficulty.

A mixture of nicotine with methyl or ethyl iodide solidifies after a short

time to a crystalline mass, containing $C_{10}H_{14}(CH_3)_2N_7I_2$, or $C_{10}H_{14}(C_2H_5)_2N_7I_2$, convertible by silver oxide into soluble bases.

By fuming nitric acid or chromic acid mixture nicotine is oxidized to nicotinic acid, $C_{10}H_7N_2O_3$, which, when distilled with lime, yields pyridine, and when heated with bromine-water to $120^\circ C.$ ($248^\circ F.$) is resolved into bromoform, carbon dioxide, nitrogen, and pyridine.

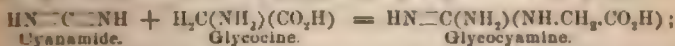
Sparteine, $C_{15}H_{26}N_2$, occurs in the common broom (*Spartium scoparium*), and is obtained therefrom by extraction with dilute sulphuric acid and distillation with potash. It is a colorless liquid, boiling at $228^\circ C.$ ($442.4^\circ F.$); dissolves sparingly in water, has a bitter taste, and acts as a narcotic. It is strongly alkaline, and has the constitution of a biacid tertiary amine.

OXYGENIZED BASES.

1. Bases related to the Ureides.—Derivatives of Guanidine.

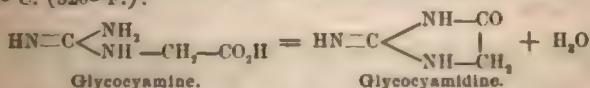
The following compounds are derived from guanidine $CH_3N_3 = HNC \equiv (NH_2)_2$ (p. 649), by the substitution of acid radicles for an atom of hydrogen.

Glycoeyamine or **Guanidacetylic Acid**, $C_3H_5N_3O_2$, is formed on mixing the aqueous solutions of glycocine and cyanamide (p. 548):



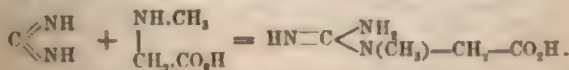
and separates in granular crystals, soluble in 120 parts of cold water, easily soluble in hot water, insoluble in alcohol and ether. It unites with bases, forming crystalline compounds. Boiled with water and lead-oxide, or with dilute sulphuric acid, it is resolved into guanidine, oxalic acid and carbonic acid.

Glycoeyamidine or **Glycolylguanidine**, $C_3H_5N_3O$, related to glycoeyamine in the same manner as hydantoïn to hydantoic acid (p. 802), is formed, as a hydrochloride, by heating the hydrochloride of glycoeyamine to $160^\circ C.$ ($320^\circ F.$):



The free base crystallizes in deliquescent laminae, having an alkaline reaction. Its hydrochloride gives a precipitate with platinic chloride.

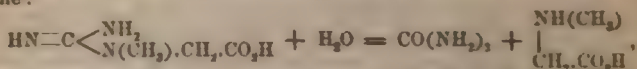
Creatine, $C_4H_7N_3O_2$, **Methylglycoeyamine**, occurs in the animal organism, especially in flesh juices, and is formed artificially, like glycoeyamine, by the union of cyanamide with methyl-glycocine (sarcosine, p. 779):



It may be prepared by macerating finely-chopped meat in cold water, boiling the extract to coagulate albumin, precipitating the phosphoric acid from the filtrate by baryta-water, and evaporating to the crystallizing point.

Creatine crystallizes in shining prisms containing 1 mol. H_2O , which they give off at 100° . It is neutral, slightly bitter, moderately soluble in boiling water, very sparingly in alcohol; forms crystalline salts containing one equivalent of acid.

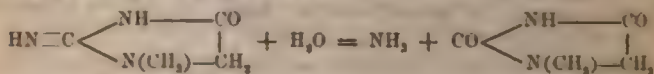
Creatine heated with acids is converted, by abstraction of H_2O , into creatinine (*infra*). By boiling with water it is resolved into urea and sarcosine:



methyl-hydantoin being also formed, and ammonia given off. Boiled with mercuric oxide, it yields methylguanidine and oxalic acid.

Creatinine, $C_4H_7N_3O$, *Methylglycocyamidine*, is an almost constant constituent of urine (0.25 per cent.), and is formed from creatine by evaporating the aqueous solution of the latter, especially in presence of acids. It crystallizes in rhombic prisms, much more soluble in water and alcohol than creatine; expels ammonia from its salts; and forms well-crystallized salts with acids. It unites also with certain salts, forming, for example, the compound $(C_4H_7N_3O)_2 \cdot \text{ZnCl}_2$, which is precipitated by zinc chloride from solutions of creatinine as a sparingly soluble crystalline powder.

Creatinine is reconverted into creatine by the action of bases, and is resolved by boiling with baryta into ammonia and methyl-hydantoin—



By boiling with mercuric oxide it is resolved, like creatine, into methylguanidine and oxalic acid.

Nearly related to the ureides are also the bases guanine, sarcine, xanthine, and carnine, which, like urea, occur in the animal organism as products of the oxidation of the tissues—and the two vegetable bases, theobromine and caffeine. The constitution of these bases is not yet established, but their relation to the ureides is shown by their products of decomposition.

Guanine, $C_5H_5N_5O$, was first obtained from guano; it has also been proved to exist in the pancreatic juice of mammalia, and in the excrement of the spider. To prepare it, guano is boiled with water and calcium hydrate until a portion of the liquid, when filtered, appears but slightly colored: the whole is then filtered, and the filtrate saturated with acetic acid, whereby the guanine is precipitated, mixed with uric acid. It is purified by solution in hydrochloric acid and precipitation by ammonia.

Guanine is a colorless, crystalline powder, insoluble in water, alcohol, ether, and ammonia, soluble in acids and solution of potash. It unites with acids forming crystallizable salts, e. g., $C_5H_5N_5O \cdot \text{HCl} + \text{Aq.}$; $2C_5H_5N_5O \cdot \text{H}_2\text{SO}_4 + 2\text{Aq.}$; $3C_5H_5N_5O \cdot 2C_2H_3O_2$; also with metallic bases and salts, e. g., $C_5H_5N_5O \cdot \text{NaHO} + 2\text{Aq.}$; $C_5H_5N_5O \cdot \text{AgNO}_3$. By oxidation with hydrochloric acid and potassium chlorate, it is converted into a mixture of guanidine and parabanic acid (799).

Xanthine, $C_5H_4N_4O_2$, is found in small quantity in many animal secretions, as in urine and blood, in the liver, and in certain urinary calculi;

It is formed artificially by the action of nitrous acid upon guanine, and of sodium amalgam on uric acid. It is a white amorphous mass, somewhat soluble in boiling water, and uniting both with acids and with bases. It dissolves easily in boiling aqueous ammonia, and silver-nitrate added to the solution throws down the compound $C_5H_7Ag_2N_4O_8 + H_2O$. This compound treated with methyl iodide yields a body isomeric with theobromine:



Sarcine or **Hypoxanthine**, $C_5H_7N_4O$, almost always accompanies xanthine in the animal organism; and is distinguished from xanthine especially by the sparing solubility of its hydrochloride. It forms needles slightly soluble in water, more soluble in acids and alkalies. From its ammoniacal solution, silver-nitrate throws down the compound $C_5H_7Ag_2N_4O + H_2O$.

Carnine, $C_7H_9N_4O_3$, occurs in extract of meat. It is pulverulent, moderately soluble in hot water, and forms a crystalline hydrochloride.

Theobromine, $C_7H_9N_4O_2$, which differs in composition from carnine by only 1 atom of oxygen, occurs in cacao beans, the seeds of *Theobroma cacao*, from which cocoa and chocolate are prepared. To extract it, the beans are boiled with water; the solution is precipitated with lead acetate, to remove extraneous matters; the filtrate is freed from lead by hydrogen sulphide, and evaporated to dryness; and the residue is treated with alcohol, which extracts the theobromine.

Theobromine is a white crystalline powder, having a bitter taste, slightly soluble in water and in alcohol, moderately soluble in aqueous ammonia. It has a neutral reaction, but unites with acids, forming crystalline salts, which are decomposed by water. From the ammoniacal solution silver nitrate throws down the compound $C_7H_7AgN_4O_2$, which, by heating to 100° with methyl iodide, is converted into methyl-theobromine, $C_7H_7(CH_3)N_4O_2$, or theine.

Theine or **Caffeine**, $C_8H_{10}N_4O_2$, *Methyl-theobromine*, occurs in the leaves and seeds of the coffee tree, in tea-leaves, in Paraguay tea (from *Ilex paraguayensis*), and in guarana, the dried pulp of the fruit of *Paullinia sorbilis*. Theine is extracted from these substances by the process above described for the preparation of theobromine: it crystallizes on cooling, and may be purified by means of animal charcoal.

Theine forms tufts of silky needles containing one mol. H_2O , slightly soluble in cold water and in alcohol, and giving off their water of crystallization at 100° . It melts at 225° C. (437° F.), and sublimes without decomposition at a higher temperature. It is a weak base, most of its salts being decomposed by water. The aurochloride and platinochloride, however, are more stable, and form orange-yellow crystals.

By the action of chlorine or nitric acid, theine is converted, with evolution of methylamine and cyanogen chloride, into amalic acid, $C_{12}H_{11}N_3O_7$, which has the composition of tetramethyl-alloxantin, $C_6(CH_3)_4N_4O_7$. It forms sparingly soluble crystals, which are colored violet-blue by alkalies. By the further action of chlorine-water, theine yields cholestrophane or dimethylparabanic acid, $C_2(C_6H_5)_2N_2O_4$ (p. 800).

Theine boiled with baryta-water, is resolved into CO_2 , and theidine or caffeine, $C_7H_{12}N_4O$, an easily soluble strongly basic compound, which is decomposed by prolonged boiling with water into sarcosine and other products.

2. Opium Bases.

Opium, the inspissated juice of the half-ripe capsules of the poppy (*Papaver somniferum*), is a very complex substance, containing a large number of bases combined with sulphuric and meconic acid. The best known of these bases are:

| | | | |
|------------|--------------------|-------------|--------------------|
| Morphine,* | $C_{17}H_{19}NO_3$ | Papaverine, | $C_{20}H_{21}NO_3$ |
| Codeine, | $C_{18}H_{21}NO_3$ | Narceine, | $C_{22}H_{25}NO_3$ |
| Thebaine, | $C_{19}H_{21}NO_3$ | Narceine, | $C_{22}H_{25}NO_3$ |

Of these, morphine and narceine are the most abundant, the first occurring in small quantity, and only in particular varieties of opium.

The bases are obtained by digesting opium with warm water, precipitating the meconic acid with calcium chloride, and leaving the concentrated filtrate to crystallize. The hydrochlorides of morphine and codeine then crystallize out first, and may be separated by treating their aqueous solution with ammonia, whereby the morphine is alone precipitated, the codeine remaining dissolved.

The mother-liquor of the morphine and codeine hydrochlorides is mixed with ammonia, which throws down narceine, together with small quantities of papaverine, and thebaine, and a resin, while narceine remains in solution.

Morphine. $C_{17}H_{19}NO_3 + H_2O$, *Morphia* or *Morphium*, is precipitated from its salts as a white powder, and crystallizes from alcohol in small but very brilliant prisms. It requires at least 500 parts of water for solution, tastes slightly bitter, and has an alkaline reaction. These effects are much more evident in the alcoholic solution. It dissolves in about 31 parts of boiling alcohol, and with great facility in dilute acids. It is also dissolved by excess of caustic potash or soda, but scarcely by excess of ammonia. When heated in the air, morphine melts, burns like a resin, and leaves a small quantity of charcoal, which easily burns away. Morphine in small doses is narcotic, in larger doses, highly poisonous.

Morphine is a tertiary mono-acid base. Its hydrochloride, $C_{17}H_{19}NO_3.HCl + 3H_2O$, crystallizes in tufts of slender needles easily soluble in water and in alcohol. The acetate, $C_{17}H_{19}NO_3.C_2H_3O_2$, is moderately soluble in water, and crystallizes in needles.

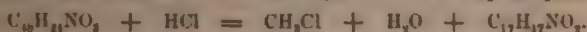
Solutions of morphine and its salts are colored dark-blue by ferric chloride; its solution in strong sulphuric acid is colored blood-red by a drop of nitric acid. Solution of iodine added to the solution of the hydrochloride throws down the periodide, $C_{17}H_{19}NO_3.I_4$. Morphine heated with potash-lye gives off methylamine.

A polymorphine, $C_{17}H_{17}NO_3$, a compound containing $1H_2O$ less than morphine, is formed when morphine is heated in a sealed tube with strong hydrochloric acid, and separates as a white powder, which turns green on contact with the air. It differs from morphine in being soluble in alcohol, ether, and chloroform, and in its physiological action, which is not narcotic, but emetic.

Codeine, $C_{18}H_{21}NO_3 = C_{17}H_{17}(CH_3)NO_3$, *Methyl-morphine*.—This base, obtained from opium as above described, crystallizes from ether in large rhombic prisms melting at $120^\circ C.$ ($240^\circ F.$). It is more soluble in water than the other opium bases; potash precipitates it from the solutions of

* It is convenient to designate organic bases by names ending in *ine*; neutral substances by names ending in *in*; e.g. *gelatin*, *albumin*, *casein*.

its salts. Heated with strong soda-lime it gives off methylamine and trimethylamine. Heated with strong hydrochloric acid to 140° – 150° C. (284° – 302° F.), it is resolved into methyl chloride and apomorphine:



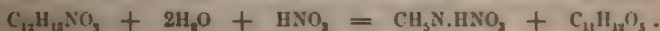
Codeine is also a tertiary monamine, forming with ethyl iodide a crystalline iodide, $C_{17}H_{21}(C_2H_5)_2NO_3 \cdot I$, converted by silver oxide into an alkaline base.

Narcotine. $C_{21}H_{23}NO_7$.—The *mare*, or insoluble portion of opium, contains much narcotine, which may be extracted by boiling with dilute acetic acid. From the filtered solution the narcotine is precipitated by ammonia, and afterwards purified by solution in boiling alcohol, and filtration through animal charcoal. Narcotine crystallizes in small, colorless, brilliant prisms, nearly insoluble in water. Its basic powers are very feeble; it is destitute of alkaline reaction, and although freely soluble in acids, does not, for the most part, form crystallizable salts.

Narcotine, treated with a mixture of dilute sulphuric acid and manganese dioxide, or a hot solution of platonic chloride, yields opianic acid (p. 923), together with basic products.

Cotarnine, $C_{17}H_{17}NO_3$, is contained in the mother-liquor from which opianic acid has crystallized; it forms a yellow crystalline mass, very soluble, of bitter taste, and feebly alkaline reaction. Its hydrochloride is a well-defined salt.

Cotarnine, gently heated with very dilute nitric acid, is converted into methylamine nitrate, and *cotarnic acid*, a bibasic acid containing $C_{11}H_{12}O_5$:

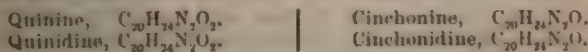


Thebaine. $C_{19}H_{21}NO_3$, *Papaverine*, $C_{20}H_{21}NO_4$, and *Narceine*, $C_{23}H_{29}NO_6$, are also contained in opium in small quantity. Thebaine forms silvery scales, melting at 193° C. (379.4° F.); insoluble in water, potash, and ammonia. Papaverine melts at 141° – 145° C. (285.8° – 293° F.).

The following bases are also found in opium, at least occasionally; *codamine*, $C_{19}H_{23}NO_3$, *lanthopine*, $C_{13}H_{25}NO_4$, *laudanine*, $C_{20}H_{23}NO_3$, *meconidine*, $C_{21}H_{23}NO_4$, *opiamine* and *porphyrosine*, but they are of small importance, and comparatively little is known respecting them.*

3. Cinchona Bases.*

The barks of the various species of cinchona contain a number of alkaloids, associated with quinic acid and cinchona-tannin. The best known of these bases are:



Quinine is found chiefly in yellow cinchona-bark (from *China regia*); cinchonine in the gray bark (from *China Huancoco*).

The bases are extracted by digesting the pulverized bark with dilute hydrochloric acid, and precipitating the filtered solution with sodium carbonate, or magnesia. The precipitate, consisting of quinine, cinchonine,

* See Hesse, *Ann. Ch. Pharm.*, clxiii. 71; Gmelin's *Handbook*, xviii. 102, 197, 199, 202, 210; *Watts's Dictionary of Chemistry*, Supplement, p. 883.

and a few other substances, is boiled with alcohol, and the solution is saturated with sulphuric acid, and evaporated. On cooling, it first deposits sulphate of quinine, and afterwards the cinchonine salt. The free bases are easily separated by ether, which dissolves only the quinine. Quinidine and cinchonidine are found in the last mother-liquors of the sulphuric acid solution.

Cinchonine crystallizes in small, brilliant, transparent, four-sided prisms. It is very slightly soluble in water, dissolves readily in boiling alcohol, and has but little taste, although its salts are excessively bitter. It is a powerful base, neutralizing acids completely, and forming a series of crystallizable salts. It turns the plane of polarization strongly to the right.

Quinine much resembles cinchonine; but does not crystallize so well: it is much more soluble in water: tastes intensely bitter; turns the plane of polarization strongly to the left.

Quinine sulphate is manufactured on a very large scale for medicinal use. It crystallizes in small white needles, which give a neutral solution. It contains $2C_{20}H_{24}N_2O_2 \cdot SO_4H_2 + 7Aq.$ Its solubility is much increased by the addition of a little sulphuric acid, whereby the acid salt, $C_{20}H_{24}N_2O_2 \cdot SO_4H_2 + 7Aq.$, is formed. Solutions of quinine sulphate exhibit a splendid blue fluorescence. On adding to the solution of a quinine salt, first chlorine-water and then ammonia, a fine green color is produced. Iodine added to a solution of quinine sulphate, forms a crystalline substance of a brilliant emerald color, which appears to have the composition $2C_{20}H_{24}N_2O_2 \cdot 3H_2SO_4 \cdot I_2 + 3Aq.$ This compound, called *Herapathite*, after its discoverer, possesses the optical properties of tourmaline.

Cinchonine and quinine yield with methyl iodide, the compounds $C_{20}H_{24}(CH_3)N_2OI$ and $C_{20}H_{24}(CH_3)N_2OI$, which are converted by silver oxide into soluble bases analogous to tetraethyl-ammonium hydroxide: they are therefore tertiary amines.

Quinidine and *Cinchonidine*, isomeric respectively with quinine and cinchonine, are obtained from commercial quinoïdine, a resinous product contained in the mother-liquors of the quinine preparation.

Quinidine (or *Cinchinine*) crystallizes in large prisms moderately soluble in alcohol, sparingly in ether. Its salts are more soluble than those of quinine. The solutions are strongly dextrogyrate. With chlorine-water and ammonia quinidine reacts like quinine.

Cinchonidine, occurring also in the bark of *China Bogota*, is very much like cinchonine. Its solutions are strongly levogyrate.

The acid sulphates of these four bases, heated first to $100^\circ C.$ to expel water of crystallization, and then to about $135^\circ C.$ ($275^\circ F.$), are converted into the sulphates of two amorphous bases, quinicine and cinchonine, isomeric with quinine and cinchonine respectively, quinicine, $C_{20}H_{24}N_2O_2$, being formed from quinine and quinidine, cinchonine, $C_{20}H_{24}N_2O_2$, from cinchonine and cinchonidine. The solutions of both of these bases are feebly dextrogyrate.

All the four bases, when distilled with caustic potash, yield bases of the chinoline series (p. 976).

4. *Strychnos Bases.*

Strychnine, $C_{21}H_{22}N_2O_2$, and **Brucine**, $C_{22}H_{28}N_2O_4$, also called *Strychnia* and *brucina*, are contained, together with several still imperfectly known bases, in *Nux vomica*, in *St. Ignatius bean*, and in *false Angustura bark*. To prepare them, *nux vomica* seeds are boiled in dilute sulphuric acid until they become soft: they are then crushed, and the expressed liquid is mixed with excess of calcium hydrate, which throws down the alkaloïds. The precipitate is boiled in spirits of wine of sp. gr. 0.850, and filtered hot. Strychnine and brucine are then deposited together in a colored and impure state, and may be separated by cold alcohol, in which the latter dissolves readily.

Pure strychnine crystallizes under favorable circumstances in small but exceedingly brilliant octohedral crystals, which are transparent and colorless. It has a very bitter, somewhat metallic taste (1 part in 1,000,000,000 parts of water is still perceptible), is slightly soluble in water, and fearfully poisonous. It dissolves in hot and somewhat dilute spirit, but not in absolute alcohol, ether, or solution of caustic alkali. This alkaloïd may be readily identified by moistening a crystal with concentrated sulphuric acid, and adding to the liquid a crystal of potassium dichromate, when a deep violet tint is produced, which disappears after some time.

Strychnine forms neutral crystalline salts, containing one equivalent of acid. The nitrate, $C_{21}H_{22}N_2O_2 \cdot NO_3H$, is sparingly soluble in water and in alcohol. Potassium thiocyanate added to the solutions throws down crystalline thiocyanate of strychnine.

Brucine, $C_{22}H_{28}N_2O_4$, crystallizes in efflorescent prisms or tables containing $4H_2O$, easily soluble in alcohol, slightly in water, insoluble in ether; also very poisonous. Strong sulphuric acid colors the solutions red, and on adding stannous chloride to the red liquid, a violet precipitate is formed. Strong sulphuric acid dissolves brucine with reddish color.

5. *Bases from various Plants.*

Veratrine or **Veratria**, $C_{32}H_{52}N_2O_8$, is obtained from the seeds of *Veratrum Sabadilla*, and from the root of *V. album*. In the pure state it is a white or yellowish-white powder, which has a sharp burning taste, is very poisonous, and in small quantities occasions violent sneezing. It is insoluble in water, but dissolves in hot alcohol, in ether, and in acids: the solution has an alkaline reaction.

Jervine, $C_{30}H_{46}N_2O_3$, occurring together with veratrine, in the root of *Veratrum album*, forms small prisms soluble in alcohol. Its salts are slightly soluble in water.

Piperine, $C_{17}H_{19}NO_3$, occurs in *Piper niger* and other kinds of pepper, from which it may be extracted by alcohol. It crystallizes in four-sided prisms, melting at 100° , easily soluble in alcohol and ether, insoluble in water; dissolves with dark-red color in strong sulphuric acid. Heated with soda-lime it gives off piperidine, and by boiling with alcoholic potash, it is resolved into piperidine and piperic acid (p. 919):



Piperidine, $C_5H_{11}N = C_5H_{10}NH$, is a liquid which boils at $106^\circ C.$ ($222.80^\circ F.$), dissolves easily in alcohol and ether, has a strong alkaline reaction,

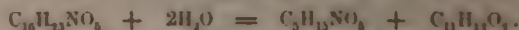
and forms neutral crystalline salts with 1 eq. of acid. It is a secondary amine, one of its hydrogen-atoms being replaceable by acid and alcoholic radicals. *Methyl-piperidine*, $C_8H_{16}N.C_2H_5$, and *ethyl-piperidine*, $C_8H_{16}N.C_2H_5$, are colorless liquids, the former boiling at $118^\circ C.$ ($244.4^\circ F.$), the latter at $280^\circ C.$ ($524.4^\circ F.$). Benzoyl-piperidine, $C_8H_{16}N.C_7H_5O$, is crystalline. Piperine is a similar derivative containing the radicle of piperic acid, $C_8H_{16}N.C_{12}H_9O_2$.

Atropine or Daturine, $C_{17}H_{23}NO_3$, occurring in the deadly nightshade (*Atropa belladonna*) and in the thorn apple (*Datura Stramonium*), crystallizes in thin prisms, melting at $90^\circ C.$ ($194^\circ F.$). It is bitter, very poisonous, and in small quantity produces dilatation of the pupil. By heating with baryta-water or hydrochloric acid, it is resolved into tropic acid (p. 913) and tropine:



Tropine is a strong mono-acid base, crystallizing from ether in tables, melting at $61^\circ C.$ ($141.8^\circ F.$).

Sinapine, $C_{16}H_{23}NO_3$, occurs in white mustard seed in the form of the cyanate, which may be dissolved out by alcohol. The base, separated from the thiocyanate or other salt by alkalies, remains dissolved, and decomposes on evaporation. By boiling the salts with alkalies, the sinapine is resolved into choline (p. 645) and sinapic acid, $C_{11}H_{13}O_3$.



Sinapic acid is bibasic, and crystallizes in thin prisms, soluble in hot water and in alcohol.

There are numerous other alkaloids, more or less known, occurring in plants; the following short notice of a few of them must suffice—

Hyoxyamine.—A white, crystallizable substance, from *Hyoxygonus nigra*. It occurs likewise in *Datura Stramonium*.

Solanine, $C_{45}H_{71}NO_{14}$ (?).—A pearly, crystalline substance, from various solanaceous plants; resolved by boiling with dilute acids into glucose and solanidine: $C_{45}H_{71}NO_{14} + 3H_2O = 3C_6H_{12}O_6 + C_{27}H_{41}NO$.

Aconitine, $C_{30}H_{47}NO_7$.—A crystalline, very poisonous alkaloid, from *Aconitum Napellus*.

Delphinine.—A yellowish, fusible substance, from the seeds of *Delphinium Staphisagria*.

Emetine.—A white and nearly tasteless powder, from *Ipecacuanha* root.

Curarine.—The arrow-poison of Central America.

Pectous Substances.

The pulp of fleshy fruits in the unripe state, also of fleshy roots and other vegetable organs, contains a substance called *pectose*, which is insoluble in water, but under the influence of acids and other reagents, is transformed into a soluble substance *pectin*, identical with that which exists in ripe fruits and imparts to their juices the property of gelatinizing when boiled.

Pectin may be obtained by boiling the pulp of carrots or turnips with a slightly acid liquid—or better, from the rinds of ripe pears, by precipitating the lime with oxalic acid, then the albuminous substances with tannic acid, and adding alcohol, whereupon the pectin separates in long threads.

as a jelly. When dry it forms an amorphous, tasteless mass, soluble in water, and precipitated therefrom by alcohol or by basic acetate of lead. On boiling the aqueous solution, the pectin is converted into parapectin, which, as well as pectin itself, is converted by boiling with dilute acids, into metapectin, which has an acid reaction, and is precipitated by strontium chloride. These three substances are said to be isomeric, and represented by the empirical formula, $C_7H_5O_2$.

According to Frémy, all vegetable tissues which contain pectose contain a ferment called pectase, similar in its mode of action to diastase and emulsin. It is an amorphous substance, which may be precipitated by alcohol from fresh carrot-juice. Under the influence of this ferment—of dilute caustic alkalis at 30° —pectin is transformed into pectosic acid, $C_{31}H_{40}O_{20} \cdot 3H_2O$, and afterwards into pectic acid, $C_{16}H_{15}O_{13} \cdot 11H_2O$, which, by prolonged boiling with water, is converted into parapectic acid, $C_{24}H_{30}O_{21} \cdot 2H_2O$. The final product of the transformation of pectous substances is metapeptic acid, $C_8H_{10}O_7 \cdot 2H_2O$, which reduces alkaline copper solutions, and is resolved by alkalis into formic and propionate acids. The composition of all these bodies is, however, very uncertain.

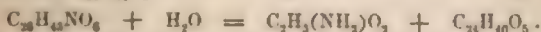
Bile Constituents.

1. **BILIARY ACIDS.**—Bile, the fluid secretion of the liver, contains—in addition to fats, mucous substances, proteids, urea, and choline—the sodium salts of two peculiar acids, called glycocholic and taurocholic; also certain coloring matters, and an aromatic alcohol called cholesterin, already described (p. 886).

Glycocholic Acid, $C_{26}H_{43}NO_6$.—When fresh ox-bile perfectly dried is exhausted with cold absolute alcohol, and mixed after filtration with ether, it first deposits a brownish, tough, resinous mass, and after some time, white crystals, consisting of the glycocholates and taurocholates of sodium and potassium. On dissolving these salts in water and adding dilute sulphuric acid, glycocholic acid separates after twenty-four hours in the crystalline state, while taurocholic acid remains dissolved.

Glycocholic acid crystallizes in white slender needles, sparingly soluble in water, easily in alcohol. It has a faint acid reaction and bitter-sweet taste. It is monobasic; its alkali-salts are very soluble in water, and have a very sweet taste. On adding to glycocholic acid a solution of sugar and then strong sulphuric acid, a purple-red coloration is produced (Pettenkofer's bile-reaction).

Glycocholic acid is resolved by boiling with alkalis into glycocine and cholic acid, $C_{24}H_{40}O_5$:

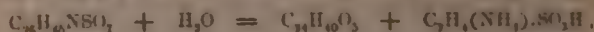


Cholic acid crystallizes in shining quadratic octohedrons containing $2\frac{1}{2}$ mol. water, soluble in alcohol and ether.

Glycocholic acid is also resolved into glycocine and cholic acid by boiling with acids, but the cholic acid is then converted, by abstraction of water, into dyslysin, $C_{24}H_{36}O_5$, an amorphous substance which is reconverted into cholic acid by boiling with alcoholic potash.

Taurocholic Acid, $C_{28}H_{45}NSO_7$, may be precipitated by basic lead acetate, after the glycocholic acid, mucus, and coloring matters have been removed by the neutral acetate. It forms slender needles, having a

sweetish-bitter taste, and easily soluble in water and in alcohol. By boiling with water it is resolved into cholic acid and taurine (p. 605).



the cholic acid being, however, for the most part converted by dehydration into dyslysin. The same decomposition takes place in the putrefaction of bile.

Pig's bile contains two acids analogous to the above, viz., hyoglycic cholic acid, $C_{22}H_{42}NO_6$, and hyotaurocholic acid, $C_{27}H_{48}NSO_6$, which are resolved by boiling with acids into hyocholic acid, $C_{22}H_{42}O_6$, and glycocine or taurine respectively.

Goose-bile contains a similar acid, $C_{26}H_{46}NSO_6$, called chenotaurocholic acid, which is resolved by alkalies into taurin and chenocholic acid, $C_{27}H_{44}O_6$.

Lithofelllic acid, $C_{20}H_{30}O_4$, an acid nearly related to the bilary acids, occurs, together with ellagic acid, in Oriental boxwood (p. 929). It may be extracted by hot alcohol, and crystallizes in short prisms, melting at $204^{\circ}C$. ($399.2^{\circ}F$.); gives, with sugar-solution and strong sulphuric acid, a purple-red color, similar to that produced with glycosidic acid.

BILE PIGMENTS.—*Bilirubin*, $C_{42}H_{58}N_2O_5$, the principal coloring matter of the bile, forms dark-red prisms, insoluble in water, sparingly soluble in alcohol and ether, easily in chloroform and carbon sulphide. It dissolves in alkalies, forming a yellowish-red solution, which, when agitated in contact with the air, yields a green precipitate of *biliverdin*, $C_{42}H_{54}N_2O_4$. *Bilifuscin*, $C_{40}H_{50}N_2O_4$, is a dark-green mass, insoluble in water and chloroform, easily soluble in alcohol.

On heating an alkaline solution of these bile-pigments with nitric acid, a green color is produced, changing to blue, violet, red, and ultimately to yellow. This reaction serves for the detection of bile.

Gelatinous Substances.

The bone-cartilages, tendons, connective tissue, and skin of the animal body dissolve, for the most part, when boiled for a long time with water, yielding a solution which solidifies, on cooling, to a transparent tremulous mass called gelatin or glutin; the non-hardening cartilages yield a similar substance, called chondrin.

These substances contain in 100 parts:

| | C | H | N | O |
|----------------|------|-----|------|------|
| Gelatin . . . | 50.0 | 6.6 | 16.3 | 23.1 |
| Chondrin . . . | 49.1 | 7.1 | 14.4 | 23.4 |

Their molecular weights and structural formulae are unknown.

Gelatin, Bone-gelatin, or Glutin, precipitated from its aqueous solution by alcohol, forms a colorless, transparent mass, without taste or smell. It swells up in cold water, and dissolves, on boiling, to a viscous liquid which solidifies to a jelly on cooling. By prolonged boiling with a small quantity of nitric acid, or, by the addition of concentrated acetic acid, the solution loses the property of gelatinizing. The aqueous solution turns the plane of polarization to the left. It is precipitated by alcohol, mercuric chloride, mercuric nitrate, and mercurous nitrate, but not by alkalis.

or by lead acetate, either neutral or basic. Tannic acid throws down, even from very dilute solutions of gelatin, a tough yellowish precipitate, consisting of a compound of the two bodies. The tissues which yield gelatin likewise unite with tannic acid, and withdraw it completely from its solutions, forming leather.

Gelatin boiled with sulphuric acid or with alkalis yields leucine and glycocine, together with other products of unknown constitution. By destructive distillation it yields several amines belonging to the fatty and pyridine series. By oxidation with MnO_2 and sulphuric acid, or with chromic acid, it yields the same products as the proteids.

Isinglass is a very pure gelatin obtained from the dried swimming bladder of the sturgeon: it dissolves in water merely warm. Size is an impure gelatin, prepared from the clippings of hides and similar matters. *Glue* is the same substance dried by exposing it in thin slices on nettings to a current of air.

Chondrin, obtained from the cartilages of the ribs and joints, is very much like gelatin, but differs from it in being precipitated from its aqueous solution by acetic acid, alum, lead acetate, and other metallic salts, but not by mercuric chloride. Its products of decomposition are, for the most part, the same as those of gelatin; with sulphuric acid, however, it yields no glycocine, but only leucine. When boiled with hydrochloric acid it yields glucose.

Silk-gelatin or Sericin, $C_{15}H_{25}N_3O_8$, is extracted from silk by boiling with water, and precipitated by alcohol as an amorphous powder. It swells up in water, dissolves on boiling, and solidifies to a jelly; is precipitated by potassium ferrocyanide, basic lead acetate, and several other metallic salts. By boiling with sulphuric acid it yields leucine, tyrosine, and amidoglyceric acid or serine (p. 757).

Fibroin, $C_{15}H_{25}N_3O_6$, the chief constituent of silk (about 66 per cent.), is obtained by repeatedly digesting silk with water at $130^\circ C.$ ($266^\circ F.$), and exhausting the residue with alcohol and ether: it then remains as a white shining mass. It dissolves in strong sulphuric acid and in alkalis, and is precipitated on saturating the solutions. When boiled with sulphuric acid it yields leucine, tyrosine, and glycocine.

Proteids or Albuminoids.

These substances form the chief part of the solid constituents of the blood, muscles, nerves, glands, and other organs of animals; they occur also in small quantities in almost every part of vegetables, and in larger quantities in the seeds. They are formed exclusively in plants, and undergo but little alteration when consumed as food and assimilated by animals.

The several bodies of this class resemble one another closely in their properties, and more especially in their percentage composition, which is comprised between the following limits:

| | | | |
|--------------------|------|----|------|
| Carbon | 52.7 | to | 54.5 |
| Hydrogen | 6.9 | " | 7.3 |
| Nitrogen | 15.4 | " | 16.5 |
| Oxygen | 20.9 | " | 23.5 |
| Sulphur | 0.8 | " | 1.6 |

These numbers may be approximately represented by the empirical formula $C_{57}H_{101}N_{15}O_{42}S$. The proteins also contain a small quantity of phosphorus, but apparently only mechanically mixed with them as calcium phosphate. Their molecular weights and constitution are not yet known, but recent investigations have thrown some light on the question, and indicate at least the direction in which its solution is to be sought. According to Hlasiwetz and Habermann, all proteins, when heated with concentrated sulphuric acid, or better, with hydrochloric acid, and a small quantity of stannous chloride, are resolved exactly into aspartic acid, glutamic acid (p. 700), leucine, tyrosine, and ammonia, and may, therefore, be regarded as formed by the combination of these substances, with elimination of water. Schützenberger, by heating proteins with barium-water to 150° (whereby $\frac{1}{5}$ of the nitrogen was evolved as ammonia), obtained essentially the same products of decomposition, and likewise intermediate products resulting from a less complete decomposition. The relative quantities of ammonia and carbon dioxide corresponded exactly with those which are evolved in the resolution of urea into $2NH_3$ and CO_2 . This result tends to show that albumin is a complex ureide, containing one fifth of its nitrogen in the form of urea.

Proteins are precipitated from solution: 1. By excess of mineral acids. 2. By potassium ferrocyanide with acetic acid or a little hydrochloric acid. 3. By acetic acid, with a considerable quantity of concentrated solution of neutral salts of the alkalis and alkaline earths, gum arabic, or dextrin. 4. When boiled with mercuric nitrate (Millon's reagent),* they give a deposit which turns red after a while, the supernatant liquors also becoming red. They rotate the plane of polarization more or less to the left.

Proteins may be conveniently divided into the following classes:

CLASS I. ALBUMINS.—Soluble in water.

1. **Serum Albumin** is the most abundant albuminous substance in animal bodies. It can be obtained tolerably pure from blood-serum by precipitation with lead acetate, washing with water, suspending the precipitated lead-compound in water, and decomposing it with carbonic acid, then by filtration a very cloudy solution of albumin is obtained.

Serum albumin forms a yellow elastic transparent substance, which when perfectly dry can be heated to 100° without change. It is soluble in water, and precipitable by alcohol: long-continued action of alcohol changes it into coagulated albumin. Its specific rotation is -56° for yellow light. It is not precipitated by carbonic, acetic, tartaric, or phosphoric acid, or by other mineral acids, when very dilute, and added in small quantity; large quantities of acid precipitate it immediately; nitric acid acts most strongly.

2. **Egg Albumin** differs from serum albumin by gradually giving a precipitate when agitated with ether, oil of turpentine also coagulates it. Serum albumin dissolves easily in strong nitric acid, whilst egg albumin is nearly insoluble therein. The specific rotation of egg albumin is -36° for yellow light.

The so-called *vitellin* contained in solution in the yolk of egg is a mixture of albumin and casein.

* Prepared by gently warming mercury with an equal quantity of concentrated acid till it is dissolved, then adding the liquid with twice its bulk of water, and leaving the precipitate to settle. The clear supernatant liquid is Millon's reagent.

3. **Plant Albumin** occurs in nearly all vegetable juices, especially in potatoes and in wheat-flour. It coagulates by heat, and bears a close resemblance to egg albumin.

CLASS II. GLOBULINS.—Insoluble in water, soluble in very dilute acids and alkalies, soluble in dilute (1 per cent.) solutions of sodium chloride and other neutral salts.

1. **Myosin.**—This substance was first separated by Kühne from other albuminous matters occurring in the protoplasmic or contractile muscular substance that causes the *rigor mortis*. To prepare it, well cut-up flesh is carefully washed with water, and the mass is then placed in a mixture of one volume of concentrated solution of common salt to two volumes of water; these are continually rubbed together and filtered through linen; the slimy filtrate is allowed to drop into a large quantity of distilled water. The myosin is redissolved in solution of sodium chloride, and reprecipitated by much water. It is insoluble in water, soluble in solution of common salt under 100° C. (500° F.), soluble in very dilute hydrochloric acid, but in this solution it passes by degrees into acid albumin or syntonin; in dilute alkali, myosin, like other albuminous matters, is soluble, being changed into albuminate. By heat it is changed into coagulated albumin. It is also coagulated by alcohol.

2. **Globulin (Paraglobulin, Paraglobin).**—When fresh blood-serum is diluted tenfold with water, and a brisk stream of carbonic acid passed through it, a fine granular precipitate is formed, which may be separated by decantation and filtration, and washed with water. The same substance may be prepared by saturating blood-serum with sodium chloride (or magnesium sulphate, etc.), as in the case of myosin. A certain amount of the salt always clings to the precipitate.

Globulin is exceedingly soluble in dilute saline solutions (from which it may be precipitated unchanged by carbonic acid gas or exceedingly dilute acids). It is insoluble in water, but dissolves when the water is saturated with oxygen, and may be precipitated by carbonic acid.

In excessively dilute alkalies globulin dissolves without alteration; in solutions containing about 1 per cent. of the alkali, it dissolves as albuminate. By dilute acids, however feeble, it is changed in solution into acid albumin. Suspended in water and heated to 70° C. (158° F.), it enters into the insoluble or coagulated state.

Globulin is present, not only in serum of blood, but also in aqueous humor, in the juice of the cornea, connective tissue, etc. Derived from the first of these sources, globulin is fibrinoplastic, i. e., it has the power of acting in concert with certain fluids (fibrinogenous) in such a manner as to give rise to fibrin (p. 991). The crystalline lens contains a substance which is not fibrinoplastic, but in many other respects closely resembles the globulin just described.

3. **Fibrinogen.**—When hydropsal fluid, pericardial fluid, or any other fluid capable of giving a clot with blood-serum or paraglobulin, is treated by the method adopted for globulin, a similar substance is produced which resembles globulin in every respect, except that the carbonic acid precipitate is more difficult to obtain and more flaky, and that the substance is more readily thrown down from the liquids in which it is formed, by a mixture of alcohol and ether; also by the fact that it is fibrinogenous, i. e., produces fibrin when mixed with fibrinoplastic globulin.

CLASS III. DERIVED ALBUMINS.—Insoluble in water, and in solutions of sodium chloride; soluble in dilute acids and alkalies.

1. **Acid-albumin.**—If a small quantity of dilute acid (hydrochloric or acetic) be added to serum- or egg-albumin, no precipitation or coagulation takes place, and on gradually raising the temperature of the mixture to 70° C. (158° F.), it will be found that coagulation at that or at a higher temperature has been entirely prevented. At the same time, the influence of the fluid on polarized light has been altered. The rotation to the left has become increased to 72°.

On carefully neutralizing the cooled mixture, the whole of the proteid matter is thrown down as a white, flocculent, frequently gelatinous precipitate. The action of the acid has converted the albumin soluble in water into a substance insoluble in water. The precipitate is very readily soluble in excess of the alkali used for neutralization, may be reprecipitated by again neutralizing with an acid, again redissolved by excess, and so on. It is also soluble in dilute solutions of alkaline carbonates. It is insoluble in sodium chloride solution, and may be precipitated from its solutions by the addition of that salt. Suspended in water and heated to 70° C. (158° F.), it enters into the coagulated or insoluble condition.

All the globulins of Class II. are readily soluble in dilute acids, but by the act of solution they are at once converted into acid-albumin, the precipitate formed by neutralization being no longer soluble in neutral saline solutions.

2. **Alkali-albumin or Albuminate. Casein.**—When albuminous substances, egg- or serum-albumin, for example, are treated with dilute caustic alkali instead of acid, coagulation by heat is similarly prevented, and the whole of the proteid may in like manner be thrown down on neutralization. Some of the bodies thus produced agree well together, and cannot be distinguished from the casein of milk, although most probably casein is not identical with artificial albuminate, and the bodies which are produced by the action of potash on different albuminous substances may differ slightly one from the other, as is evident in the difference of their rotatory action on polarized light.

Casein occurs most plentifully in the milk of animal feeders, and is best obtained from milk by precipitating with crystalline magnesium sulphate, filtering and washing with a concentrated solution of salt, then dissolving the precipitate in water; the butter is filtered off, and the clear solution precipitated by dilute acetic acid.

Dried casein and albuminate are yellow, transparent, and hygroscopic, swelling up in water, but not dissolving. When precipitated in a floccy state, they dissolve easily in water if it contains a little alkali. The precipitate which forms on neutralizing the alkaline solution, dissolves easily in an excess of acetic acid or dilute hydrochloric acid. On the addition of an excess of mineral acid, or on neutralization with an alkali, these solutions give a precipitate.

The neutral or feebly alkaline albuminate, and casein in alkaline solution, are precipitated in the cold by alcohol: when hot they are dissolved. By fusion with potassium hydrate, casein yields valeric and butyric acids, besides other products.

The most striking property of casein is its coagulability by certain animal membranes, as is seen in the process of cheese-making, in preparing the *curd*, the coagulation being effected by an infusion of the stomach of the calf called *rennet*.

Plant-casein, or *Legumin*, is found chiefly in the seeds of leguminous fruits, from the juice of which it may be precipitated by acetic acid or by rennet,

CLASS IV.—Fibrin.—Insoluble in water; sparingly soluble in dilute acids and alkalis, and in neutral saline solutions.

This is the substance to which the clotting of blood is due. It may be obtained by washing blood-clots, or more readily by stirring with a bundle of twigs, blood just shed, before it has had time to clot. The fibrin, which adheres in layers to the twigs, may then be stripped off and washed till perfectly white. The formation of fibrin is due to the contact of fibrinoplastin and fibrinogenous substance. When these two substances come into contact in any fluid, they combine, quickly or slowly, according to the greater or lesser quantity of each substance in the fluid, to form fibrin.

Fibrin differs from all other solid proteids in having a filamentous structure, and in possessing remarkable elasticity. It is insoluble in water, dilute hydrochloric acid, and aqueous sodium chloride, but dissolves at 40° C. (104° F.) in aqueous potassium nitrate.

Plant-fibrin occurs as an insoluble substance in plants, especially in the seeds of cereal grasses. When wheat-flour is stirred up to a paste with water, and kneaded for some time, the starch granules and soluble albumin are removed, and there remains a tenacious mass called gluten; and by boiling this substance with dilute alcohol to remove vegetable gelatin (gluten) and extracting the fats with ether, the plant-fibrin is obtained in the form of a grayish-white, tough, elastic mass. It dissolves in very dilute hydrochloric acid, and in dilute alkalis, and is precipitated from these solutions by neutral salts, and by acetic acid. By boiling with dilute sulphuric acid, plant-fibrin is resolved into leucine, tyrosine, and glutamic acid.

CLASS V. Coagulated Protoid.—Coagulated albumin is formed from albumin, syntonin, fibrin, myosin, etc., by heating their neutral solutions to boiling, or by the action of alcohol. Egg albumin is also changed into coagulated albumin by strong hydrochloric acid and by ether. The albuminates, and also casein, when precipitated by neutralization, pass into coagulated albumin when heated. The coagulated albuminous substances are insoluble in water, alcohol, and other indifferent fluids, scarcely soluble in dilute potash, soluble with great difficulty in ammonia. In acetic acid they swell up, and gradually dissolve. They are mostly insoluble in dilute hydrochloric acid; but when pepsin is also present at blood heat, they change first into syntonin, and then into peptone. They are dissolved by strong hydrochloric acid, and by caustic potash they are changed into albuminates.

CLASS VI. Peptones.—By the action of the acid gastric juice, all albuminous substances are changed into bodies called peptones. These are found only in the stomach and in the contents of the small intestines. They can no longer be detected in the chyle. They are highly diffusible, easily soluble in water, insoluble in alcohol or ether; but alcohol separates them with difficulty from the watery solution; when precipitated they remain unchanged even after boiling. They are not precipitated either by acids or by alkalis. Acetic acid and potassium ferrocyanide give no precipitate; but corrosive sublimate and lead acetate with ammonia give precipitates.

The reactions of the several proteids above described may be tabulated as follows:—

Soluble in water:

| | | | |
|---|---|---|-----------|
| Aqueous solutions not coagulated by boiling | . | . | PEPTONES. |
| Aqueous solutions coagulated by boiling | . | . | ALBUMINS. |

Insoluble in water:

| | | | |
|--|---|---|-------------|
| Soluble in a 1 p. c. solution of sodium chloride | . | . | GLUCULANES. |
|--|---|---|-------------|

Insoluble :

Soluble in hydrochloric acid (0.1 p. c.) in the cold :

| | | |
|-----------------------------------|---|----------|
| Soluble in hot spirit | { | ALKALI- |
| | | ALBUMIN. |
| Insoluble in hot spirit | { | ACID- |
| | | ALBUMIN. |

Insoluble in hydrochloric acid (0.1 p. c.) in the cold :

| | | | |
|---|---|---------|------------|
| Soluble in hydrochloric acid (0.1 p. c.) at 60° | { | FIBRIN. | |
| Insoluble in hydrochloric acid (0.1 p. c.) at 60° : | | { | COAGULATED |
| insoluble in strong acids ; soluble in gastric juice | | | ALBUMIN. |

Substances related to the Proteids.

Hæmoglobin, 54.2 oxygen, 7.2 hydrogen, 0.42 iron, 16.0 nitrogen, 21.5 oxygen, and 0.7 sulphur ; also called *Hæmatoglobulin* and *Hæmatocytallin*.—This substance forms the chief part of the red globules of the blood of vertebrata ; usually it is obtained in an amorphous condition, but from the blood of some animals—as, for example, dogs, cats, rats, mice, and many fish—it can be separated in the crystalline form. Red crystals can be obtained from dog's blood by mixing the defibrinated blood with an equal quantity of water, adding 1 volume of alcohol to 4 volumes of the diluted blood, and leaving it at rest at 60° or lower. After 24 hours the hæmoglobin separates in small violet-red rhombic octohedrons. After drying over sulphuric acid it forms a brick-red powder. It dissolves in cold water, forming a red solution, from which it is precipitated in the crystalline form by alcohol. At ordinary temperatures the solution decomposes and turns brown.

The aqueous solution of hæmoglobin (or of blood) exhibits in its spectrum two absorption-bands situated between the Fraunhofer lines D and E (in the yellow and green).

Hæmoglobin unites with certain gases forming peculiar unstable compounds. The solution containing oxygen has a deep red color, the solution free from oxygen is dark purple (arterial and venous blood) ; the absorption-bands are exhibited only by the oxygenated solution. Carbon monoxide displaces the oxygen, and forms with the hæmoglobin a compound which, on addition of alcohol, separates in bluish crystals. This appears to be the cause of the deleterious action of carbon monoxide on animals.

Oxygenated hæmoglobin is resolved by dilute acids or alkalis into two proteids, fatty acids, and a coloring matter called *hematin*, which in the dry state is a dark blue powder. It contains 9 per cent. of iron, and appears to have the composition $C_{24}H_{24}FeN_4O_8$.

When hæmoglobin (or blood) is warmed with strong acetic acid and solution of common salt, a substance called *hematin* separates in yellowish red microscopic rhombic crystals, the formation of which serves as a delicate indication of the presence of blood.

Related to the proteids are also many *ferments*, such as *emulsin* or *synaptase*, occurring in almonds ; *diastase* (p. 532), which is formed from vegetable fibrin in the germination of seeds, and is characterized by the property of converting starch and dextrin into sugar ; *myrosin* from mustard-seeds (p. 547) ; *ptyalin*, the ferment of saliva, which also converts starch into dextrin and sugar ; *pepsin*, which is contained in gastric juice, and possesses the power, in conjunction with hydrochloric acid, of dissolving the insoluble proteids and converting them into peptones.

Mucin is the chief constituent of animal mucus, and is precipitated by alcohol and dilute acetic acid.

The horny substances of horns, nails, hoofs, hairs, feathers, and the epidermis, are also nearly related to the proteids, having indeed the same composition, except that they contain more sulphur (2-5 p. c.). They dissolve easily in alkalies, with formation of sulphides. Nitric acid turns them yellow. Boiled with dilute sulphuric acid they yield leucine and tyrosine.

Brain Constituents.

When brain or spinal marrow is boiled with water, creatine, inosite, lactic acid, uric acid, and other substances, it dissolves, and from the residue ether extracts fats, cholesterin (p. 886), cerebrin, and lecithin. On cooling the solution, the two latter substances are first deposited, and may be separated by cold ether, which dissolves only the lecithin. The so-called *protagon* is a mixture of cerebrin and lecithin.

Cerebrin or Cerebric Acid, $C_{17}H_{33}NO_3$, is a light amorphous powder, without taste or smell; swells up like starch when boiled with water, and is converted by boiling with dilute acids into a saccharine substance, and other products.

Lecithin, $C_{42}H_{84}NPO_6$, is widely diffused in the animal organism, occurring especially in the brain nerves, yolk of eggs, blood-corpuscles, etc. It is best prepared by exhausting egg-yolk with a mixture of alcohol and ether, evaporating the ether, adding an alcoholic solution of platinic chloride, decomposing the yellow platinochloride, $(C_{42}H_{84}NPO_6Cl)_2.PtCl_6$, with hydrogen sulphide, and evaporating the filtrate.

Lecithin is a waxy, indistinctly crystalline mass, which dissolves in alcohol and ether, and swells up in water, forming an opalescent solution or emulsion, from which it is precipitated by various salts of the alkali-metals. It unites both with bases and with acids.

By boiling with acids, or with baryta-water, lecithin is resolved into choline, glycerophosphoric acid, palmitic acid, and oleic acid.



APPENDIX.

HYDROMETER TABLES.

COMPARISON OF THE DEGREES OF BAUME'S HYDROMETER WITH THE REAL SPECIFIC GRAVITIES.

1. For Liquids heavier than Water.

| Degrees. | Specific Gravity. | Degrees. | Specific Gravity. | Degrees. | Specific Gravity. |
|----------|-------------------|----------|-------------------|----------|-------------------|
| 0 | 1.000 | 26 | 1.206 | 52 | 1.520 |
| 1 | 1.007 | 27 | 1.216 | 53 | 1.535 |
| 2 | 1.013 | 28 | 1.225 | 54 | 1.551 |
| 3 | 1.020 | 29 | 1.235 | 55 | 1.567 |
| 4 | 1.027 | 30 | 1.246 | 56 | 1.583 |
| 5 | 1.034 | 31 | 1.256 | 57 | 1.600 |
| 6 | 1.041 | 32 | 1.267 | 58 | 1.617 |
| 7 | 1.048 | 33 | 1.277 | 59 | 1.634 |
| 8 | 1.056 | 34 | 1.288 | 60 | 1.652 |
| 9 | 1.063 | 35 | 1.299 | 61 | 1.670 |
| 10 | 1.070 | 36 | 1.310 | 62 | 1.689 |
| 11 | 1.078 | 37 | 1.321 | 63 | 1.708 |
| 12 | 1.085 | 38 | 1.333 | 64 | 1.727 |
| 13 | 1.094 | 39 | 1.345 | 65 | 1.747 |
| 14 | 1.101 | 40 | 1.357 | 66 | 1.767 |
| 15 | 1.109 | 41 | 1.369 | 67 | 1.788 |
| 16 | 1.118 | 42 | 1.381 | 68 | 1.809 |
| 17 | 1.126 | 43 | 1.395 | 69 | 1.831 |
| 18 | 1.134 | 44 | 1.407 | 70 | 1.854 |
| 19 | 1.143 | 45 | 1.420 | 71 | 1.877 |
| 20 | 1.152 | 46 | 1.434 | 72 | 1.900 |
| 21 | 1.160 | 47 | 1.448 | 73 | 1.944 |
| 22 | 1.169 | 48 | 1.462 | 74 | 1.949 |
| 23 | 1.178 | 49 | 1.476 | 75 | 1.974 |
| 24 | 1.188 | 50 | 1.490 | 76 | 2.000 |
| 25 | 1.197 | 51 | 1.495 | | |

APPENDIX.

2. Baumé's Hydrometer for Liquids lighter than Water.

| Degrees. | Specific Gravity. | Degrees. | Specific Gravity. | Degrees. | Specific Gravity. |
|----------|-------------------|----------|-------------------|----------|-------------------|
| 10 | 1.000 | 27 | 0.896 | 44 | 0.811 |
| 11 | 0.998 | 28 | 0.890 | 45 | 0.807 |
| 12 | 0.986 | 29 | 0.885 | 46 | 0.802 |
| 13 | 0.980 | 30 | 0.880 | 47 | 0.798 |
| 14 | 0.973 | 31 | 0.874 | 48 | 0.794 |
| 15 | 0.967 | 32 | 0.869 | 49 | 0.789 |
| 16 | 0.960 | 33 | 0.864 | 50 | 0.785 |
| 17 | 0.954 | 34 | 0.859 | 51 | 0.781 |
| 18 | 0.948 | 35 | 0.854 | 52 | 0.777 |
| 19 | 0.942 | 36 | 0.849 | 53 | 0.773 |
| 20 | 0.936 | 37 | 0.844 | 54 | 0.768 |
| 21 | 0.930 | 38 | 0.839 | 55 | 0.764 |
| 22 | 0.924 | 39 | 0.834 | 56 | 0.760 |
| 23 | 0.918 | 40 | 0.830 | 57 | 0.757 |
| 24 | 0.913 | 41 | 0.825 | 58 | 0.753 |
| 25 | 0.907 | 42 | 0.820 | 59 | 0.749 |
| 26 | 0.901 | 43 | 0.816 | 60 | 0.745 |

These two tables are on the authority of Francœur; they are taken from the *Handwörterbuch der Chemie* of Liebig, Poggendorf, and Wöhler. Baumé's hydrometer is very commonly used on the Continent, especially for liquids heavier than water. For lighter liquids the hydrometer of Cartier is often employed in France. Cartier's degrees differ but little from those of Baumé.

In the United Kingdom, Twaddell's hydrometer is a good deal used for dense liquids. This instrument is so graduated that the real specific gravity can be deduced by an extremely simple method from the degree of the hydrometer; namely, by multiplying the latter by 5, and adding 1000, the sum is the specific gravity, water being 1000. Thus 10° Twaddell indicates a specific gravity of 1050, or 1.05; 90° Twaddell, 1450, or 1.45.

In the Customs and Excise, Sikes's hydrometer is used.

TABLE III.

ABSTRACT OF REGNAULT'S TABLE OF THE MAXIMUM TENSION OF WATER-VAPOR,
AT DIFFERENT TEMPERATURES, EXPRESSED IN MILLIMETERS OF MERCURY.

| Temperature. | | Tension,
millimeters. | Temperature. | | Tension,
millimeters. |
|--------------|------------|--------------------------|--------------|---------|--------------------------|
| — 32° C. | — 25.6° F. | 0.320 | 100° C. | 212° F. | 760.000 |
| 30 | 22.0 | 0.386 | 105 | 221 | 906.410 |
| 25 | 13.0 | 0.605 | 110 | 230 | 1075.370 |
| 20 | 4.0 | 0.927 | 115 | 239 | 1269.410 |
| 15 | + 5.0 | 1.400 | 120 | 248 | 1491.280 |
| 10 | 14.0 | 2.093 | 125 | 257 | 1743.880 |
| ■ | 23.0 | 3.113 | 130 | 266 | 2030.280 |
| 0 | 32.0 | 4.600 | 135 | 275 | 2353.730 |
| + 5 | 41.0 | 6.534 | 140 | 284 | 2717.630 |
| 10 | 50.0 | 9.165 | 145 | 293 | 3125.55 |
| 15 | 59.0 | 12.699 | 150 | 302 | 3581.23 |
| 20 | 68.0 | 17.391 | 155 | 311 | 4088.56 |
| 25 | 77.0 | 23.550 | 160 | 320 | 4651.02 |
| 30 | 86.0 | 31.548 | 165 | 329 | 5274.54 |
| 35 | 95.0 | 41.827 | 170 | 338 | 5961.66 |
| 40 | 104.0 | 54.906 | 175 | 347 | 6717.43 |
| 45 | 113.0 | 71.391 | 180 | 356 | 7546.39 |
| 50 | 122.0 | 91.982 | 185 | 365 | 8453.23 |
| 55 | 131.0 | 117.478 | 190 | 374 | 9442.70 |
| 60 | 140.0 | 148.791 | 195 | 383 | 10519.63 |
| 65 | 149.0 | 186.945 | 200 | 392 | 11688.96 |
| 70 | 158.0 | 233.093 | 205 | 401 | 12955.66 |
| 75 | 167.0 | 288.517 | 210 | 410 | 14324.80 |
| 80 | 176.0 | 354.643 | 215 | 419 | 15801.33 |
| 85 | 185.0 | 433.041 | 220 | 428 | 17390.36 |
| 90 | 194.0 | 525.450 | 225 | 437 | 19097.04 |
| 95 | 203.0 | 633.778 | 230 | 446 | 20926.40 |

APPENDIX.

WEIGHTS AND MEASURES.

| | | |
|-------------------|---|--------------------|
| 480·0 grains Troy | = | 1 oz. Troy. |
| 437·5 " | = | 1 oz. Avoirdupois. |
| 7000·0 " | = | 1 lb. Avoirdupois. |
| 5760·0 " | = | 1 lb. Troy. |

| | | |
|--|---------|-------|
| 1 gallon contains of water at 60° (15°·50) | 70,000· | grain |
| ($\frac{1}{4}$ of gallon)..... | 8,750· | " |
| One fluid-ounce ($\frac{1}{16}$ of pint)..... | 437·5 | " |
| The pint equals 34·66 cubic inches. | | |

The French *kilogramme* = 15,433·6 grains, or 2·679 lb. Troy, or
2·205 lb. avoirdupois.

| | | |
|----------------------|---|-----------------|
| The <i>gramme</i> | = | 15·4336 grains. |
| " <i>decigramme</i> | = | 1·5434 " |
| " <i>centigramme</i> | = | 0·1543 " |
| " <i>milligramme</i> | = | 0·0154 " |

| | | |
|----------------------------|---|------------------|
| The <i>mètre</i> of France | = | 39·37 inches. |
| " <i>decimètre</i> | = | 3·937 " |
| " <i>centimètre</i> | = | 0·894 " |
| " <i>millimètre</i> | = | 0·0394 " |

MEASURES OF LENGTH

| | In English Inches. | In English Feet = 12 Inches. | In English Yards = 3 Feet. | In English Fathoms = 2 Feet. | In English Miles = 1760 yards. |
|------------------|--------------------|------------------------------|----------------------------|------------------------------|--------------------------------|
| Millimètre | 0.03937 | 0.0022809 | 0.0010936 | 0.0005458 | 0.0000006 |
| Centimètre | 0.39371 | 0.0228090 | 0.0109363 | 0.0054582 | 0.0000062 |
| Décimètre | 3.93704 | 0.3280839 | 0.1093633 | 0.0545816 | 0.0000621 |
| Mètre | 39.37079 | 3.2808392 | 1.0936331 | 0.5458165 | 0.0006214 |
| Décamètre | 393.70790 | 32.8083920 | 10.9363310 | 5.4581655 | 0.0062138 |
| Hectomètre | 3937.07900 | 328.0839200 | 109.3633100 | 54.5816550 | 0.0621382 |
| Kilomètre | 39370.79000 | 3280.8392000 | 1093.6331000 | 545.8165500 | 0.6213824 |
| Myriomètre | 393707.90000 | 32808.3920000 | 10936.3310000 | 5458.1655000 | 6.2138244 |

1 Inch = 2.540004 Centimètres.
1 Foot = 30.47949 Decimètres.

1 Yard = 0.91438348 Metre.
1 Mile = 1.6093440 Kilomètre.

MEASURES OF SURFACE.

| | In English Square Feet. | In English Sq. Yards = 9 Square Feet. | In English Poles = 27.25 Sq. Feet. | In English Rods = 10.560 Sq. Feet. | In English Acres = 48,560 Sq. Feet. |
|------------------------------------|-------------------------|---------------------------------------|------------------------------------|------------------------------------|-------------------------------------|
| Centiare or sq. mètre | 10.7642993 | 1.1960233 | 0.0360383 | 0.00998457 | 0.0002471143 |
| Are or 100 sq. mètres | 1076.4299342 | 119.6032360 | 3.6582900 | 0.098845724 | 0.0247114310 |
| Hectare or 10,000 sq. mètres | 107642.9934183 | 11960.3326020 | 395.3928959 | 9.884572998 | 2.4711430996 |

1 Square Inch = 6.4516000 Square Centimètres.
1 Square Foot = 0.2999684 Square Decimètres.

1 Square Yard = 0.83605716 Square Mètre or Centiare.
1 Acre = 0.404671021 Hectare.

TABLE

FOR CONVERTING DEGREES OF THE CENTIGRADE THERMOMETER INTO
DEGREES OF FAHRENHEIT'S SCALE.

| Cent. | Fah. | Cent. | Fah. | Cent. | Fah. |
|-------|------|-------|------|-------|------|
| -100° | ... | -55° | ... | -10° | ... |
| 99 | ... | 54 | ... | 9 | ... |
| 98 | ... | 53 | ... | 8 | ... |
| 97 | ... | 52 | ... | 7 | ... |
| 96 | ... | 51 | ... | 6 | ... |
| 95 | ... | 50 | ... | 5 | ... |
| 94 | ... | 49 | ... | 4 | ... |
| 93 | ... | 48 | ... | 3 | ... |
| 92 | ... | 47 | ... | 2 | ... |
| 91 | ... | 46 | ... | 1 | ... |
| 90 | ... | 45 | ... | 0 | ... |
| 89 | ... | 44 | ... | +1 | ... |
| 88 | ... | 43 | ... | 2 | ... |
| 87 | ... | 42 | ... | 3 | ... |
| 86 | ... | 41 | ... | 4 | ... |
| 85 | ... | 40 | ... | 5 | ... |
| 84 | ... | 39 | ... | 6 | ... |
| 83 | ... | 38 | ... | 7 | ... |
| 82 | ... | 37 | ... | 8 | ... |
| 81 | ... | 36 | ... | 9 | ... |
| 80 | ... | 35 | ... | 10 | ... |
| 79 | ... | 34 | ... | 11 | ... |
| 78 | ... | 33 | ... | 12 | ... |
| 77 | ... | 32 | ... | 13 | ... |
| 76 | ... | 31 | ... | 14 | ... |
| 75 | ... | 30 | ... | 15 | ... |
| 74 | ... | 29 | ... | 16 | ... |
| 73 | ... | 28 | ... | 17 | ... |
| 72 | ... | 27 | ... | 18 | ... |
| 71 | ... | 26 | ... | 19 | ... |
| 70 | ... | 25 | ... | 20 | ... |
| 69 | ... | 24 | ... | 21 | ... |
| 68 | ... | 23 | ... | 22 | ... |
| 67 | ... | 22 | ... | 23 | ... |
| 66 | ... | 21 | ... | 24 | ... |
| 65 | ... | 20 | ... | 25 | ... |
| 64 | ... | 19 | ... | 26 | ... |
| 63 | ... | 18 | ... | 27 | ... |
| 62 | ... | 17 | ... | 28 | ... |
| 61 | ... | 16 | ... | 29 | ... |
| 60 | ... | 15 | ... | 30 | ... |
| 59 | ... | 14 | ... | 31 | ... |
| 58 | ... | 13 | ... | 32 | ... |
| 57 | ... | 12 | ... | 33 | ... |
| 56 | ... | 11 | ... | 34 | ... |

APPENDIX.

LIST OF THERMOMETER SCALES (continued).

| Cent. | Fah. | Cent. | Fah. | Cent. | Fah. | | |
|-------|------|--------|------|---------|------|---------|-----|
| +35° | ... | +96-0° | ... | +185-0° | ... | +275-0° | ... |
| 36 | ... | 96-8 | ... | 185-8 | ... | 275-8 | ... |
| 37 | ... | 98-6 | ... | 188-6 | ... | 278-6 | ... |
| 38 | ... | 100-4 | ... | 190-4 | ... | 280-4 | ... |
| 39 | ... | 102-2 | ... | 192-2 | ... | 282-2 | ... |
| 40 | ... | 104-0 | ... | 194-0 | ... | 284-0 | ... |
| 41 | ... | 105-8 | ... | 195-8 | ... | 285-8 | ... |
| 42 | ... | 107-6 | ... | 197-6 | ... | 287-6 | ... |
| 43 | ... | 109-4 | ... | 199-4 | ... | 289-4 | ... |
| 44 | ... | 111-2 | ... | 201-2 | ... | 291-2 | ... |
| 45 | ... | 113-0 | ... | 203-0 | ... | 293-0 | ... |
| 46 | ... | 114-8 | ... | 204-8 | ... | 294-8 | ... |
| 47 | ... | 116-6 | ... | 206-6 | ... | 296-6 | ... |
| 48 | ... | 118-4 | ... | 208-4 | ... | 298-4 | ... |
| 49 | ... | 120-2 | ... | 210-2 | ... | 300-2 | ... |
| 50 | ... | 122-0 | 100 | 212-0 | ... | 302-0 | ... |
| 51 | ... | 123-8 | 101 | 213-8 | ... | 303-8 | ... |
| 52 | ... | 125-6 | 102 | 215-6 | ... | 305-6 | ... |
| 53 | ... | 127-4 | 103 | 217-4 | ... | 307-4 | ... |
| 54 | ... | 129-2 | 104 | 219-2 | ... | 309-2 | ... |
| 55 | ... | 131-0 | 105 | 221-0 | ... | 311-0 | ... |
| 56 | ... | 132-8 | 106 | 222-8 | ... | 312-8 | ... |
| 57 | ... | 134-6 | 107 | 224-6 | ... | 314-6 | ... |
| 58 | ... | 136-4 | 108 | 226-4 | ... | 316-4 | ... |
| 59 | ... | 138-2 | 109 | 228-2 | ... | 318-2 | ... |
| 60 | ... | 140-0 | 110 | 230-0 | ... | 320-0 | ... |
| 61 | ... | 141-8 | 111 | 231-8 | ... | 321-8 | ... |
| 62 | ... | 143-6 | 112 | 233-6 | ... | 323-6 | ... |
| 63 | ... | 145-4 | 113 | 235-4 | ... | 325-4 | ... |
| 64 | ... | 147-2 | 114 | 237-2 | ... | 327-2 | ... |
| 65 | ... | 149-0 | 115 | 239-0 | ... | 329-0 | ... |
| 66 | ... | 150-8 | 116 | 240-8 | ... | 330-8 | ... |
| 67 | ... | 152-6 | 117 | 242-6 | ... | 332-6 | ... |
| 68 | ... | 154-4 | 118 | 244-4 | ... | 334-4 | ... |
| 69 | ... | 156-2 | 119 | 246-2 | ... | 336-2 | ... |
| 70 | ... | 158-0 | 120 | 248-0 | ... | 338-0 | ... |
| 71 | ... | 159-8 | 121 | 249-8 | ... | 339-8 | ... |
| 72 | ... | 161-6 | 122 | 251-6 | ... | 341-6 | ... |
| 73 | ... | 163-4 | 123 | 253-4 | ... | 343-4 | ... |
| 74 | ... | 165-2 | 124 | 255-2 | ... | 345-2 | ... |
| 75 | ... | 167-0 | 125 | 257-0 | ... | 347-0 | ... |
| 76 | ... | 168-8 | 126 | 258-8 | ... | 348-8 | ... |
| 77 | ... | 170-6 | 127 | 260-6 | ... | 350-6 | ... |
| 78 | ... | 172-4 | 128 | 262-4 | ... | 352-4 | ... |
| 79 | ... | 174-2 | 129 | 264-2 | ... | 354-2 | ... |
| 80 | ... | 176-0 | 130 | 266-0 | ... | 356-0 | ... |
| 81 | ... | 177-8 | 131 | 267-8 | ... | 357-8 | ... |
| 82 | ... | 179-6 | 132 | 269-6 | ... | 359-6 | ... |
| 83 | ... | 181-4 | 133 | 271-4 | ... | 361-4 | ... |
| 84 | ... | 183-2 | 134 | 273-2 | ... | 363-2 | ... |

APPENDIX.

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TABLE OF THERMOMETER SCALES (*continued*).

| Fah. | Cent. | Fah. | Cent. | Fah. |
|-------------|-------|-------------|-------|-------------|
| ... +365.0° | +230° | ... +446.0° | +275° | ... +527.0° |
| ... 366.8 | 231 | ... 447.8 | 276 | ... 528.8 |
| ... 368.6 | 232 | ... 449.6 | 277 | ... 530.6 |
| ... 370.4 | 233 | ... 451.4 | 278 | ... 532.4 |
| ... 372.2 | 234 | ... 453.2 | 279 | ... 534.2 |
| ... 374.0 | 235 | ... 455.0 | 280 | ... 536.0 |
| ... 375.8 | 236 | ... 456.8 | 281 | ... 537.8 |
| ... 377.6 | 237 | ... 458.6 | 282 | ... 539.6 |
| ... 379.4 | 238 | ... 460.4 | 283 | ... 541.4 |
| ... 381.2 | 239 | ... 462.2 | 284 | ... 543.2 |
| ... 383.0 | 240 | ... 464.0 | 285 | ... 545.0 |
| ... 384.8 | 241 | ... 465.8 | 286 | ... 546.8 |
| ... 386.6 | 242 | ... 467.6 | 287 | ... 548.6 |
| ... 388.4 | 243 | ... 469.4 | 288 | ... 550.4 |
| ... 390.1 | 244 | ... 471.2 | 289 | ... 552.2 |
| ... 392.0 | 245 | ... 473.0 | 290 | ... 554.0 |
| ... 393.8 | 246 | ... 474.8 | 291 | ... 555.8 |
| ... 395.6 | 247 | ... 476.6 | 292 | ... 557.6 |
| ... 397.4 | 248 | ... 478.4 | 293 | ... 559.4 |
| ... 399.2 | 249 | ... 480.2 | 294 | ... 561.2 |
| ... 401.0 | 250 | ... 482.0 | 295 | ... 563.0 |
| ... 402.8 | 251 | ... 483.8 | 296 | ... 564.8 |
| ... 404.6 | 252 | ... 485.6 | 297 | ... 566.6 |
| ... 406.4 | 253 | ... 487.4 | 298 | ... 568.4 |
| ... 408.2 | 254 | ... 489.2 | 299 | ... 570.2 |
| ... 410.0 | 255 | ... 491.0 | 300 | ... 572.0 |
| ... 411.8 | 256 | ... 492.8 | 301 | ... 573.8 |
| ... 413.6 | 257 | ... 494.6 | 302 | ... 575.6 |
| ... 415.4 | 258 | ... 496.4 | 303 | ... 577.4 |
| ... 417.2 | 259 | ... 498.2 | 304 | ... 579.2 |
| ... 419.0 | 260 | ... 500.0 | 305 | ... 581.0 |
| ... 420.8 | 261 | ... 501.8 | 306 | ... 582.8 |
| ... 422.6 | 262 | ... 503.6 | 307 | ... 584.6 |
| ... 424.4 | 263 | ... 505.4 | 308 | ... 586.4 |
| ... 426.2 | 264 | ... 507.2 | 309 | ... 588.2 |
| ... 428.0 | 265 | ... 509.0 | 310 | ... 590.0 |
| ... 429.8 | 266 | ... 510.8 | 311 | ... 591.8 |
| ... 431.6 | 267 | ... 512.6 | 312 | ... 593.6 |
| ... 433.4 | 268 | ... 514.4 | 313 | ... 595.4 |
| ... 435.2 | 269 | ... 516.2 | 314 | ... 597.2 |
| ... 437.0 | 270 | ... 518.0 | 315 | ... 599.0 |
| ... 438.8 | 271 | ... 519.8 | 316 | ... 600.8 |
| ... 440.6 | 272 | ... 521.6 | 317 | ... 602.6 |
| ... 442.4 | 273 | ... 523.4 | 318 | ... 604.4 |
| ... 444.2 | 274 | ... 525.2 | 319 | ... 606.2 |

TABLE VII.

WEIGHT OF ONE CUBIC CENTIMETER OF ATMOSPHERIC AIR, IN GRAMS, AT DIFFERENT TEMPERATURES, FOR EVERY 5 DEGREES FROM 0 TO 300° C. AT 760 MM. (EVERY 9 DEGREES FROM 32° TO 572° F.)

| | | Difference. | | | | Difference. | |
|-------|--------|-------------|----|---------|---------|-------------|----|
| 0° C. | 32° F. | 0.001293 | | 155° C. | 311° F. | 0.000824 | 10 |
| 5 | 41 | 0.001270 | 23 | 160 | 320 | 0.000815 | 9 |
| 10 | 50 | 0.001248 | 22 | 165 | 329 | 0.000806 | 9 |
| 15 | 59 | 0.001226 | 22 | 170 | 338 | 0.000797 | 9 |
| 20 | 68 | 0.001205 | 21 | 175 | 347 | 0.000788 | 9 |
| 25 | 77 | 0.001185 | 20 | 180 | 356 | 0.000779 | 9 |
| 30 | 86 | 0.001165 | 20 | 185 | 365 | 0.000770 | 9 |
| 35 | 95 | 0.001146 | 19 | 190 | 374 | 0.000762 | 8 |
| 40 | 104 | 0.001128 | 18 | 195 | 383 | 0.000754 | 8 |
| 45 | 113 | 0.001111 | 17 | 200 | 392 | 0.000746 | 8 |
| 50 | 122 | 0.001094 | 17 | 205 | 401 | 0.000738 | 8 |
| 55 | 131 | 0.001077 | 17 | 210 | 410 | 0.000730 | 8 |
| 60 | 140 | 0.001060 | 17 | 215 | 419 | 0.000722 | 8 |
| 65 | 149 | 0.001044 | 16 | 220 | 428 | 0.000715 | 7 |
| 70 | 158 | 0.001029 | 15 | 225 | 437 | 0.000708 | 7 |
| 75 | 167 | 0.001014 | 15 | 230 | 446 | 0.000701 | 7 |
| 80 | 176 | 0.001000 | 14 | 235 | 455 | 0.000694 | 7 |
| 85 | 185 | 0.000986 | 14 | 240 | 464 | 0.000687 | 7 |
| 90 | 194 | 0.000972 | 14 | 245 | 473 | 0.000680 | 7 |
| 95 | 203 | 0.000959 | 13 | 250 | 482 | 0.000674 | 6 |
| 100 | 212 | 0.000946 | 13 | 255 | 491 | 0.000668 | 6 |
| 105 | 221 | 0.000933 | 13 | 260 | 500 | 0.000662 | 6 |
| 110 | 230 | 0.000921 | 12 | 265 | 509 | 0.000656 | 6 |
| 115 | 239 | 0.000909 | 12 | 270 | 518 | 0.000650 | 6 |
| 120 | 248 | 0.000898 | 11 | 275 | 527 | 0.000644 | 6 |
| 125 | 257 | 0.000887 | 11 | 280 | 536 | 0.000638 | 6 |
| 130 | 266 | 0.000876 | 11 | 285 | 545 | 0.000632 | 6 |
| 135 | 275 | 0.000865 | 11 | 290 | 554 | 0.000626 | 6 |
| 140 | 284 | 0.000854 | 11 | 295 | 563 | 0.000621 | 5 |
| 145 | 293 | 0.000844 | 10 | 300 | 572 | 0.000616 | 5 |
| 150 | 302 | 0.000834 | 10 | | | | |

The column of Differences is intended to facilitate the calculation of the intermediate values. Thus, to find the weight of 1 cub. cent. of air for 52°, we must add to the weight for 50° two-fifths of the difference (17) between this and the number for 55°: thus

$$\begin{array}{rcl} \text{Weight of 1 cub. cent. of air at } 50^\circ & = & 0.001094 \\ \text{Add } \frac{2}{5} \text{ of } 17 & & = \quad \quad 7 \end{array}$$

$$\text{Weight of 1 cub. cent. of air at } 55^\circ = 0.01101$$

TABLE VIII.

1

FOR THE CALCULATION OF $1 + 0.00367 t$. (See page 71.)

| t | | t | | t | | t | | t | | t | | t | |
|-----|---------|-----|---------|-----|---------|-----|---------|-----|---------|-----|--|-----|--|
| 1 | 0.99634 | 31 | 0.89785 | 61 | 0.81708 | 91 | 0.74964 | 121 | 0.69249 | | | | |
| 2 | 0.99271 | 32 | 0.89490 | 62 | 0.81464 | 92 | 0.74758 | 122 | 0.69073 | | | | |
| 3 | 0.98911 | 33 | 0.89197 | 63 | 0.81221 | 93 | 0.74554 | 123 | 0.68899 | | | | |
| 4 | 0.98553 | 34 | 0.88906 | 64 | 0.80979 | 94 | 0.74351 | 124 | 0.68725 | | | | |
| 5 | 0.98198 | 35 | 0.88617 | 65 | 0.80740 | 95 | 0.74148 | 125 | 0.68552 | | | | |
| 6 | 0.97845 | 36 | 0.88330 | 66 | 0.80501 | 96 | 0.73947 | 126 | 0.68380 | | | | |
| 7 | 0.97495 | 37 | 0.88044 | 67 | 0.80264 | 97 | 0.73747 | 127 | 0.68209 | | | | |
| 8 | 0.97148 | 38 | 0.87761 | 68 | 0.80068 | 98 | 0.73548 | 128 | 0.68038 | | | | |
| 9 | 0.96803 | 39 | 0.87479 | 69 | 0.79794 | 99 | 0.73350 | 129 | 0.67869 | | | | |
| 10 | 0.96460 | 40 | 0.87199 | 70 | 0.79561 | 100 | 0.73153 | 130 | 0.67700 | | | | |
| 11 | 0.96120 | 41 | 0.86921 | 71 | 0.79329 | 101 | 0.72957 | 131 | 0.67532 | | | | |
| 12 | 0.95782 | 42 | 0.86645 | 72 | 0.79099 | 102 | 0.72762 | 132 | 0.67365 | | | | |
| 13 | 0.95446 | 43 | 0.86370 | 73 | 0.78870 | 103 | 0.72568 | 133 | 0.67199 | | | | |
| 14 | 0.95113 | 44 | 0.86097 | 74 | 0.78642 | 104 | 0.72376 | 134 | 0.67034 | | | | |
| 15 | 0.94782 | 45 | 0.85826 | 75 | 0.78416 | 105 | 0.72184 | 135 | 0.66870 | | | | |
| 16 | 0.94454 | 46 | 0.85556 | 76 | 0.78191 | 106 | 0.71993 | 136 | 0.66706 | | | | |
| 17 | 0.94127 | 47 | 0.85289 | 77 | 0.77967 | 107 | 0.71803 | 137 | 0.66543 | | | | |
| 18 | 0.93803 | 48 | 0.85022 | 78 | 0.77745 | 108 | 0.71615 | 138 | 0.66380 | | | | |
| 19 | 0.93482 | 49 | 0.84758 | 79 | 0.77523 | 109 | 0.71427 | 139 | 0.66219 | | | | |
| 20 | 0.93162 | 50 | 0.84495 | 80 | 0.77304 | 110 | 0.71240 | 140 | 0.66059 | | | | |
| 21 | 0.92844 | 51 | 0.84234 | 81 | 0.77085 | 111 | 0.71055 | 141 | 0.65899 | | | | |
| 22 | 0.92529 | 52 | 0.83974 | 82 | 0.76867 | 112 | 0.70870 | 142 | 0.65740 | | | | |
| 23 | 0.92216 | 53 | 0.83716 | 83 | 0.76651 | 113 | 0.70686 | 143 | 0.65582 | | | | |
| 24 | 0.91905 | 54 | 0.83460 | 84 | 0.76436 | 114 | 0.70503 | 144 | 0.65424 | | | | |
| 25 | 0.91596 | 55 | 0.83205 | 85 | 0.76222 | 115 | 0.70321 | 145 | 0.65268 | | | | |
| 26 | 0.91289 | 56 | 0.82952 | 86 | 0.76010 | 116 | 0.70140 | 146 | 0.65112 | | | | |
| 27 | 0.90984 | 57 | 0.82700 | 87 | 0.75798 | 117 | 0.69960 | 147 | 0.64957 | | | | |
| 28 | 0.90682 | 58 | 0.82450 | 88 | 0.75588 | 118 | 0.69781 | 148 | 0.64802 | | | | |
| 29 | 0.90381 | 59 | 0.82201 | 89 | 0.75379 | 119 | 0.69603 | 149 | 0.64648 | | | | |
| 30 | 0.90082 | 60 | 0.81954 | 90 | 0.75171 | 120 | 0.69425 | 150 | 0.64495 | | | | |

APPENDIX.

TABLE

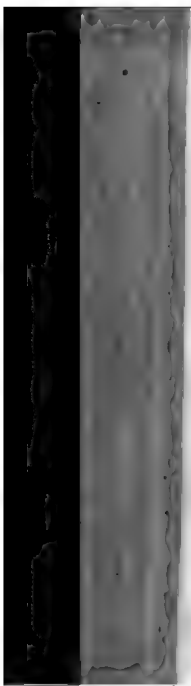
OF THE PROPORTION BY WEIGHT OF ABSOLUTE OR REAL ALCOHOL IN 100 PARTS
OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES. (TOWNES.)

| Sp. Gr. at 60°
(15°5C.). | Per cent.
of real
Alcohol. | Sp. Gr. at 60°
(15°5C.). | Per cent.
of real
Alcohol. | Sp. Gr. at 60°
(15°5C.). | Per cent.
of real
Alcohol. |
|-----------------------------|----------------------------------|-----------------------------|----------------------------------|-----------------------------|----------------------------------|
| 0.9991 | 0.5 | 0.9511 | 34 | 0.8769 | 68 |
| 0.9981 | 1 | 0.9490 | 35 | 0.8745 | 69 |
| 0.9965 | 2 | 0.9470 | 36 | 0.8721 | 70 |
| 0.9947 | 3 | 0.9452 | 37 | 0.8696 | 71 |
| 0.9930 | 4 | 0.9434 | 38 | 0.8672 | 72 |
| 0.9914 | 5 | 0.9416 | 39 | 0.8649 | 73 |
| 0.9896 | 6 | 0.9396 | 40 | 0.8625 | 74 |
| 0.9884 | 7 | 0.9378 | 41 | 0.8603 | 75 |
| 0.9869 | 8 | 0.9356 | 42 | 0.8581 | 76 |
| 0.9855 | 9 | 0.9336 | 43 | 0.8557 | 77 |
| 0.9841 | 10 | 0.9314 | 44 | 0.8533 | 78 |
| 0.9828 | 11 | 0.9292 | 45 | 0.8508 | 79 |
| 0.9815 | 12 | 0.9270 | 46 | 0.8483 | 80 |
| 0.9802 | 13 | 0.9249 | 47 | 0.8459 | 81 |
| 0.9789 | 14 | 0.9228 | 48 | 0.8434 | 82 |
| 0.9778 | 15 | 0.9206 | 49 | 0.8408 | 83 |
| 0.9766 | 16 | 0.9184 | 50 | 0.8382 | 84 |
| 0.9753 | 17 | 0.9160 | 51 | 0.8357 | 85 |
| 0.9741 | 18 | 0.9135 | 52 | 0.8331 | 86 |
| 0.9728 | 19 | 0.9113 | 53 | 0.8305 | 87 |
| 0.9716 | 20 | 0.9090 | 54 | 0.8279 | 88 |
| 0.9704 | 21 | 0.9069 | 55 | 0.8254 | 89 |
| 0.9691 | 22 | 0.9047 | 56 | 0.8228 | 90 |
| 0.9678 | 23 | 0.9025 | 57 | 0.8199 | 91 |
| 0.9668 | 24 | 0.9001 | 58 | 0.8172 | 92 |
| 0.9652 | 25 | 0.8979 | 59 | 0.8145 | 93 |
| 0.9638 | 26 | 0.8956 | 60 | 0.8118 | 94 |
| 0.9623 | 27 | 0.8932 | 61 | 0.8089 | 95 |
| 0.9609 | 28 | 0.8908 | 62 | 0.8061 | 96 |
| 0.9593 | 29 | 0.8886 | 63 | 0.8031 | 97 |
| 0.9578 | 30 | 0.8863 | 64 | 0.8001 | 98 |
| 0.9560 | 31 | 0.8840 | 65 | 0.7969 | 99 |
| 0.9544 | 32 | 0.8816 | 66 | 0.7938 | 100 |
| 0.9528 | 33 | 0.8793 | 67 | | |

TABLE

THE PROPORTION BY VOLUME OF ABSOLUTE OR REAL ALCOHOL IN 100 VOLUMES OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES (RAY-LUSSAC) AT 59° F. (15° C.)

| 100 vol. Spirits. | | 100 vol. Spirits. | | 100 vol. Spirits. | |
|-------------------|-------------------------------|-------------------|------------------------------|-------------------|-------------------------------|
| Spec. Grav. | Contain vol. of real Alcohol. | Spec. Grav. | Contain vol. of real Alcohol | Spec. Grav. | Contain vol. of real Alcohol. |
| 1.0000 | 0 | 0.9608 | 34 | 0.8956 | 68 |
| 0.9985 | 1 | 0.9594 | 35 | 0.8932 | 69 |
| 0.9970 | 2 | 0.9581 | 36 | 0.8907 | 70 |
| 0.9956 | 3 | 0.9567 | 37 | 0.8882 | 71 |
| 0.9942 | 4 | 0.9553 | 38 | 0.8857 | 72 |
| 0.9929 | 5 | 0.9538 | 39 | 0.8831 | 73 |
| 0.9916 | 6 | 0.9523 | 40 | 0.8805 | 74 |
| 0.9903 | 7 | 0.9507 | 41 | 0.8779 | 75 |
| 0.9891 | 8 | 0.9491 | 42 | 0.8753 | 76 |
| 0.9878 | 9 | 0.9474 | 43 | 0.8726 | 77 |
| 0.9867 | 10 | 0.9457 | 44 | 0.8699 | 78 |
| 0.9855 | 11 | 0.9440 | 45 | 0.8672 | 79 |
| 0.9844 | 12 | 0.9422 | 46 | 0.8645 | 80 |
| 0.9833 | 13 | 0.9404 | 47 | 0.8617 | 81 |
| 0.9822 | 14 | 0.9386 | 48 | 0.8589 | 82 |
| 0.9812 | 15 | 0.9367 | 49 | 0.8560 | 83 |
| 0.9802 | 16 | 0.9348 | 50 | 0.8531 | 84 |
| 0.9792 | 17 | 0.9329 | 51 | 0.8502 | 85 |
| 0.9782 | 18 | 0.9309 | 52 | 0.8472 | 86 |
| 0.9773 | 19 | 0.9289 | 53 | 0.8442 | 87 |
| 0.9763 | 20 | 0.9269 | 54 | 0.8411 | 88 |
| 0.9753 | 21 | 0.9248 | 55 | 0.8379 | 89 |
| 0.9742 | 22 | 0.9227 | 56 | 0.8346 | 90 |
| 0.9732 | 23 | 0.9206 | 57 | 0.8312 | 91 |
| 0.9721 | 24 | 0.9185 | 58 | 0.8278 | 92 |
| 0.9711 | 25 | 0.9163 | 59 | 0.8242 | 93 |
| 0.9700 | 26 | 0.9141 | 60 | 0.8206 | 94 |
| 0.9690 | 27 | 0.9119 | 61 | 0.8168 | 95 |
| 0.9679 | 28 | 0.9096 | 62 | 0.8128 | 96 |
| 0.9668 | 29 | 0.9073 | 63 | 0.8086 | 97 |
| 0.9657 | 30 | 0.9050 | 64 | 0.8042 | 98 |
| 0.9645 | 31 | 0.9027 | 65 | 0.8006 | 99 |
| 0.9633 | 32 | 0.9004 | 66 | 0.7947 | 100 |
| 0.9621 | 33 | 0.8980 | 67 | | |



INDEX.

| PAGE | Acid: | PAGE | Acid: | PAGE | |
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| Absorption of gases..... | 145 | amidobarbituric..... | 799 | capric..... | 798 |
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nic..... | 859 | caproic..... | 796 |
| Acetaminine..... | 648 | amidobenzonic..... | 899 | caprylic..... | 797 |
| Acenaphthene..... | 950 | amidobutyric..... | 780 | carbacetoxylic..... | 798 |
| Acenaphthylene..... | 950 | amidocaproic..... | 781 | carbamio..... | 818, 784 |
| Acetal..... | 606 | amidoglutaric..... | 760 | carbanilic..... | 841 |
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